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## PHILIPPINE FIBERS AND FIBROUS SUBSTANCES: THEIR SUITABILITY FOR PAPER MAKING. PART III (CONCLUSION).

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*(From the Chemical Laboratory, Bureau of Science, Manila, P. I.)*

### INTRODUCTION.

The gradual but certain decrease in the available supply of the leading paper makers' raw material at the present time is further emphasized, by recent compilations concerning the American pulp wood industry. Some of the more important considerations brought out in a circular report on wood used for pulp [1] in 1905 are:

First. The increase in the quantity consumed, 3,192,223 cords being used during 1905, or a gain of 60.7 per cent over the corresponding figures for 1899.

Second. The increased use of chemical processes for the reduction of wood to paper pulp. In 1905 the proportions were approximately 66 per cent of chemical and 34 per cent of mechanical pulp; these percentages representing a gain of 74.7 per cent for the chemical process as against one of 39.4 per cent for the mechanical during six years.

Third. The greatly increased use of woods other than spruce and poplar, and a more general utilization of waste products from lumbering industries. Such wood species as hemlock, fir, southern, pitch and

[1] Hale, H. M.: *U. S. Dept. Agriculture, Forest Service Circ.* (1906), No. 44.

jack pines and even the hardwoods such as beach and maple, are now being employed, while slabs, sawdust and veneer cores are also being considered.

Fourth. An increase of approximately 75 per cent is also shown in the amount of pulp wood imported. This importation consists of 645,428 cords of Canadian spruce and poplar.

Fifth. The estimated length of time during which the supply will be available is given as twenty-one years.

The United States Forest Service has established a laboratory at Boston, Massachusetts, for a further investigation of the woods mentioned above as well as of other varieties and also of the waste materials, and the following quotation serves to explain the reason for its existence.

> To supply the enormous demand for the sulphite product more than 1,500,000 cords of wood are used annually. Nearly four-fifths of this amount is spruce. A rapid diminution in the supply of standing spruce and a consequent marked increase in its cost are the results of this great and growing demand. Therefore, the principal object of the laboratory is to experiment on the pulp-making possibilities of other woods.[2]

The experiments to be conducted in the Boston laboratory are intended to include the investigation of a large number of American woods and waste products; their applicability to the sulphite process of treatment; a microscopic study of the fibers and the distribution of samples of pulp and handmade sheets of paper made therefrom.

Generally speaking, the species of woods best suited for paper pulp should possess the following characteristics:

First. They should be soft, but of a resistant nature, and they should possess long, fine, parallel fibers.

Second. They should be light in weight and colorless or nearly so. The species which have the distinct heart- and sap-wood may be employed, if the distinction is not too pronounced.

Third. They should be but moderately resinous with a comparatively thin bark, and they should be relatively free from knots and unsound portions.

The above requirements seem to be met by a sufficient number of Philippine forest trees to warrant a study of their pulpmaking possibilities. Authentically identified specimens of the different woods, together with data as to their distribution, description and physical properties, were furnished by Dr. H. N. Whitford of the Philippine Bureau of Forestry and by Dr. Foxworthy of the botanical section of the Biological Laboratory, and the botanical identifications were made by Elmer D. Merrill, botanist of the Bureau of Science.

[2] *Forestry and Irrigation*, Wash. (1906), 12, 8.

TABLE NO. 1.—*Tree species proposed.*

| Botanical name. | Common name. | Specific gravity. | Weight per cubic foot. | Ash. | Remarks. |
|---|---|---|---|---|---|
| | | | *Kilos.*[a] | *Per cent.* | |
| Shorea contorta | White lauan | 0.446 | 12.56 | 0.89 | Moderately resinous. |
| Parkia roxburghii | Cupang | .285 | 8.03 | 2.08 | Non-resinous. |
| Anisoptera vidaliana | Mayapis | 399 | 11.24 | .83 | Do. |
| Alstonia scholaris | Dita | | 12.72 | .99 | Do. |
| Sandoricum vidalianum | Santol | | 16.36 | 1.12 | Do. |

[a] 1 kilo = 2.2 pounds.

## PHILIPPINE WOODS.

### LAUAN (*Shorea* sp.).

*Structural qualities.*—Lauan is a light and soft wood which takes a fair polish; the pith rays are fine but distinct, in radial section they are very prominent as horizontal lines or patches of a darker color than that of the surrounding wood; this dark color is due to resin contained in the pith-ray cells. The vessels are of medium size, often filled with gummy material; wood parenchyma is present, but of irregular distribution. The resin canals are small and scattered, often forming distinct, white, concrete lines.

*Appearance, color and grain.*—Both heart-wood and sap-wood of lauan are of a light-brown to whitish shade. The wood is straight, but of rather coarse grain.

*Uses.*—Lauan wood is employed in light and temporary construction. It is also used in cabinet making, in inferior furniture, and for small boats.

*Provinces leading in production.*—Negros Occidental, Bulacan, Bataan, Leyte and Zambales.

*Remarks.*—This is the most widely distributed tree in the Philippine forests. It is found in limited numbers in every type of lowland forest excepting the swamps, and it is also present in the foothills. Lauan has a tall and regular bole. The young trees are but slightly buttressed, but the old ones often show this development to a great degree. Several different kinds of wood are marketed under the name of lauan, the classification being as red and white. The red lauans are undoubtedly distinct in species from the true white lauan (*Shorea contorta* Vid.). There are at least two white lauans found in the Provinces of Mindoro, Bataan and Zambales, and another species (*Shorea squamata* F.-Vill.) is obtained from Negros, this variety is also locally known as *almon*. The tree designated as *malaanonang* (*Shorea malaanonan* Blume) and found scattered through the forests of Rizal and Bulacan Provinces also greatly resembles the poorer grades of lauan both in appearance and structure. It is much lighter in color than any of the commercial red lauans, and from its structure it should be considered as being useful for fiber production in the same manner as is the true white lauan.

CUPANG (*Parkia roxburghii* Don.).

Cupang is a light and soft wood. It is not durable and rots quickly; there is no distinction between sap- and heart-wood; its color is white or whitish. It is coarse grained, splitting more or less regularly; its odor is pronouncedly mephitic when it is fresh or when it is partially rotted, it is less pronounced when the wood is dry.

The vessels are of medium size, each surrounded by a collar of whitish cells; the pith rays are small but distinct, they are lighter in color than the surrounding tissue.

*Distribution.*—Cupang is probably found in lowland forests in every province of the Archipelago; it also occurs in India and throughout Malaysia.

*Uses.*—Cupang has no commercial use at the present time. It was formerly employed in the manufacture of matches, but its use was discontinued because of its odor.

*Remarks.*—Both *lauan* and *cupang* are free from knots from base to crown. Cupang grows to large diameter, with a smooth, straight cylindrical bole, which is often quite short. Usually a clear length of 40 to 55 feet terminates in a much branched crown.

MAYAPIS (*Anisoptera* sp.).

*Structural qualities.*—Mayapis is a light, soft wood and is not durable. In structure it very much resembles lauan, however it is distinctly coarser grained. Its vessels are slightly larger and more numerous and its pith rays are rather more distinct.

*Appearance, color and grain.*—Mayapis is yellowish-white in color and coarse grained.

*Uses.*—It is used in light and temporary construction.

*Provinces leading in production.*—Laguna, Tayabas, Bataan and Cagayan.

*Common names.*—Mayapis, palosapis, etc.

*Remarks.*—The tree which yields most of the lumber known as mayapis is probably *Anisoptera vidaliana* Brandis, although some other closely related species may also be known as mayapis or palosapis. This tree has a long, straight, clean bole with a small taper, the clear lengths varying from 50 to 80 feet. Its average diameter is about 20 inches.

DITA (*Alstonia scholaris* R. Br.).

Dita is a light and soft wood weighing 28 pounds per cubic foot; it seasons badly and it rapidly becomes moldy if seasoned in the log.

*Appearance, color and grain.*—There is no distinction between sap- and heart-wood; it has a white, even grain which is fine and straight. The pores are medium sized; the pith rays fine and irregularly distributed, with numerous intermediate extremely fine rays; there are many fine, wavy concentric lines at unequal distances. The wood has a very bitter taste; it is easy to work and is used for light furniture of various sorts and for the manufacture of matches.

*Alstonia scholaris* is a very large, evergreen tree, with smooth bark and straight clear bole. It is found in old clearings.

*Distribution.*—Dita is widely distributed throughout the Archipelago and also extends from India to the Philippines.

*Remarks.*—Dita is furnished by *Alstonia scholaris* R. Br. and by no other species.

SANTOL (*Sandoricum* sp.).

A moderately hard and heavy wood, weighing 16.4 kilos (36 pounds) per cubic foot. The sap-wood is gray, the heart-wood faintly reddish, resembling the color of hemlock. It is close and straight grained, very easy to work and it takes a fine polish. The wood has a camphor-like odor when first cut. The pores are small and the medullary rays fine.

*Distribution.*—The tree is very common in cultivation and in old clearings, also in lowland forests; it is found throughout the Philippines and in the Indo-Malayan region.

*Remarks.*—The scientific designation is *Sandoricum indicum* Cav., but the very similar wood *malasantol* is common in the forest and is furnished by the closely related *Sandoricum vidalii* Merr.

Other woods worthy of mention, but upon which no work has been done are *taluto* (*Pterocymbium tinctorium* Merr.), *malapapaya* (*Polyscias nodosa* Seem.), *papaya* and *balete* and other species of the genus *Ficus, Grewia* sp., etc. All of these are of common occurrence, are very soft and light and are white or nearly so in color. They all mold very quickly if allowed to cure in the log.

DATA ON THE STAND OF CUPANG, LAUAN AND MAYAPIS IN BATAAN PROVINCE.[3]

On the west coast, the basin drained by the Binonangan River comprises approximately 6,120 acres. The topography of this area is such that lumbering operations can easily be carried on. The distance from the coast to the most remote timber in this basin is about 6 miles. The area is well forested, except for a narrow strip on the seacoast where the timber is small and scattered. The principal wood species found on this area are panao, tanguile, lauan, guijo, mayapis and cupang. The cupang, among the pulp woods, covers only the lower elevations up to 900 feet, an area of approximately 3,900 acres, while the lauan and mayapis are distributed over the whole region.

The estimated total stand of the three woods is given as—

| | Cubic feet. |
|---|---|
| Cupang | 1,870,720 |
| Lauan | 1,578,960 |
| Mayapis | 1,040,400 |
| Total | 4,490,080 |

These figures represent only the merchantable stand in the basin, of trees of these species of 20 inches or more in diameter after making an average deduction of 20 per cent for unsound timber; hence 5,000,000 cubic feet of pulp wood may be obtained from this small area.

The yield tables[4] for the merchantable stand of timber on 4,590 hectares (11,339 acres) of public forest on the eastern coast of Mindoro

[3] Bryant, R. C.: *Rep. Bu. Forestry*, P. I., (1901–1902).

[4] Merrit, M. L., and Whitford, H. N.: *Phil. Bu. Forestry* (1906); 6.

show a yield of 14,060,778 cubic feet, cutting to a diameter limit of 40 centimeters (16 inches); of this amount 6,453,368 cubic feet is white lauan.

### THE SHRINKING OF THE VARIOUS WOODS ON BARKING.

Experiments to determine the shrinkage of the various woods in barking gave the following results:

TABLE No. 2.—*Green wood containing 30 to 40 per cent of moisture—blocks one-foot in length varying 15 to 20 centimeters in diameter.*

| Kind of wood. | Weight. | | Loss. |
|---|---|---|---|
| | Before barking. | After barking. | |
| | *Kilos.* | *Kilos.* | *Per cent.* |
| Lauan | 2.695 | 2.443 | 9.3 |
| Cupang | 5.430 | 4.800 | 11.6 |
| Mayapis | 7.587 | 6.740 | 11.00 |
| Dita | 8.061 | 6.670 | 17.25 |
| Santol | 8.969 | 8.012 | 10.67 |

One cord of green spruce, containing 37 per cent of moisture and cut in 4-foot lengths, weighed 2,001 kilos (4,440 pounds); after barking it was 1,622 kilos (3,570 pounds) or 19.5 per cent shrinkage.[5]

TABLE No. 3.—*Dimensions of the ultimate fibers of some Philippine woods.*

[Table by Dr. Foxworthy.]

| Name. | Length. | | | Diameter. | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Total. | | | Lumen. | | |
| | Maximum. | Average. | Minimum. | Maximum. | Average. | Minimum. | Maximum. | Average. | Minimum. |
| | *mm.* | *mm.* | *mm.* | *mm.* | *mm.* | *mm.* | *mm.* | *mm.* | *mm.* |
| Lauan (Shorea contorta) | 2.28 | 1.94 | 1.13 | 0.026 | 0.022 | 0.017 | 0.017 | 0.014 | 0.009 |
| Mayapis (Anisoptera vidaliana) | 2.62 | 1.92 | 1.16 | .030 | .023 | .019 | .0092 | .0058 | .0031 |
| Cupang (Parkia roxburgii) | 1.80 | 1.15 | .86 | .038 | .029 | .021 | .026 | .020 | .014 |
| Dita (Alstonia scholaris) | 1.85 | 1.27 | .80 | .041 | .0355 | .025 | .025 | .016 | .010 |
| Spruce[6] | 4.54 | 3.15 | 1.67 | .043 | .037 | .034 | .029 | .0195 | .003 |

[5] Griffin and Little: Chem. Paper Making (1894), 141.

[6] Sulphite pulp manufactured by Willamette Pulp and Paper Company, Oregon City, Oregon.

TABLE No. 4.—*Proximate analyses of Philippine woods and some commercial pulp woods.*

| Kind of wood. | Water. | Aqueous extract. | Alcohol ether extract. | Cellulose. | Incrusting matter. | Ash. |
|---|---|---|---|---|---|---|
| | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| **PHILIPPINE WOODS.** | | | | | | |
| Lauan | 11.23 | 3.85 | 2.72 | 61.71 | 19.57 | 0.89 |
| Mayapis | 11.50 | 4.50 | 1.20 | 55.73 | 28.24 | .83 |
| Cupang | 13.33 | 3.45 | 1.17 | 60.56 | 19.41 | 2.03 |
| Dita | 10.41 | 4.19 | .60 | 49.94 | 33.87 | .99 |
| **SOME COMMERCIAL PULP WOODS.**[7] | | | | | | |
| Scotch pine | 12.87 | 4.05 | 1.63 | 53.27 | 28.18 | |
| Block poplar | 12.10 | 2.88 | 1.37 | 62.77 | 20.88 | |
| Silver fir | 13.87 | 1.26 | .97 | 56.99 | 26.91 | |
| Bass-wood | 10.10 | 3.56 | 3.93 | 53.09 | 29.32 | |
| Spruce[8] | 11.31 | 4.83 | 3.28 | 52.96 | 35.41 | 0.32 |
| | 11.48 | | | 53.08 | 35.19 | .25 |
| | 11.26 | | | 52.98 | 35.46 | .30 |

SODA WOOD PULPS.

One-kilo lots (2.2 pounds) of wood were barked, chipped and cooked in the model digestor, washed, screened and molded into 7 by 10 inch boards. These were first air-dried and weighed, then repulped and beaten in a small hollander, bleached and formed into unsized handmade sheets.

TABLE No. 5.—*Experiments with lauan.*

| Experiment No. | Caustic soda solution. | Caustic soda calculated on weight of material. | Duration of digestion. | Pressures carried. | Yield of pulp. | | Bleaching powder consumed. | Loss of weight in bleaching. |
|---|---|---|---|---|---|---|---|---|
| | | | | | Unbleached. | Bleached. | | |
| | *Per cent.* | *Per cent.* | *Hours.* | *Atmospheres.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 10 | 25 | 9 | 6 | 40.9 | | | |
| 2 | 7.5 | 22.5 | 11 | 6 | 42.37 | 40 | 17.1 | 5.69 |
| 3 | 5 | 20 | 5 | 5 (7½) | 45.2 | 40.3 | 18.8 | 10.8 |
| 4 | 3.75 | 15 | 10 | 6–8 | 45.28 | | | |
| 5 | 3.5 | 12.5 | 10 | 6–8 | 48.6 | | | |

[7] Müller, Hugo: Die Pflanzenfaser, Leipz. (1873), 150.

[8] Analyses by Griffin and Little.

*Remarks.*—The conditions of experiment 3, namely, a 5 per cent (6° to 7° Baumé) liquor and five hours' digestion at 7 to 8 atmospheres' (105 to 120 pounds) pressure produced a well-boiled pulp, comparatively free from screenings. In experiment 4, a weaker liquor accomplished the same result in double the time, at a slightly increased pressure. Experiment 5 produced a coarse pulp, very brown and badly contaminated with shive. Experiment 1 showed evidence of too caustic a treatment.

TABLE No. 6.—*Experiments with cupang.*

| Experiment No. | Caustic soda solution. | Caustic soda calculated on weight of material. | Duration of digestion. | Pressures carried. | Yield of pulp. | | Bleaching powder consumed. | Loss of weight in bleaching. |
|---|---|---|---|---|---|---|---|---|
| | | | | | Unbleached. | Bleached. | | |
| | *Per cent.* | *Per cent.* | *Hours.* | *Atmospheres.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 7.5 | 25 | 8 | 7 | 41.91 | ---------- | ---------- | ---------- |
| 2 | 6 | 20 | 10 | 6 | 43.71 | 40.3 | 16.5 | 7.8 |
| 3 | 4.7 | 20 | 8 | 7 | 44.97 | 40.2 | 18.4 | 10.6 |
| 4 | 3.75 | 15 | 8 | 6–8 | 48.4 | ---------- | ---------- | ---------- |
| 5 | 3.5 | 12.5 | 8 | 6–8 | 50.4 | ---------- | ---------- | ---------- |

*Remarks.*—Under similar conditions of treatment, cupang pulps more easily than lauan and with a little better yield. The pulp resembles poplar, in length of fiber and ease of treatment although it is somewhat harder to bleach.

TABLE No. 7.—*Experiments with mayapis.*

| Experiment No. | Caustic soda solution. | Caustic soda calculated on weight of material. | Duration of digestion. | Pressures carried. | Yield of pulp. | | Bleaching powder consumed. | Loss of weight in bleaching. |
|---|---|---|---|---|---|---|---|---|
| | | | | | Unbleached. | Bleached. | | |
| | *Per cent.* | *Per cent.* | *Hours.* | *Atmospheres.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 10 | 22 | 5–6 | 5 | 38.5 | ---------- | ---------- | ---------- |
| 2[a] | 6.25 | 20 | 10 | 6–7 | 41.85 | 40.7 | 9.9 | 2.74 |
| 3[b] | 5 | 20 | 5 | 6–7 | 42.5 | 41 | 12 | 3.53 |
| 4 | 4 | 17.5 | 5 | 6–7 | 44 | 41.19 | 15.4 | 2.81 |

[a] Good white color. [b] Yellowish color.

*Remarks.*—Mayapis is one of the most promosing of the Philippine pulp woods. It is even lighter in color than white lauan and has a considerably longer fiber than cupang. A yield of 40 to 45 per cent of easily bleached pulp may be expected by digestion with alkaline liquors.

Dita wood is too short fibered and weak to be of much value for paper pulp. It is briefly considered here because of its wide distribution and abundance in the Philippines and because it would yield the bark which

contains the most widely known and important Filipino drug as a by-product. The alkaloids from dita bark are being investigated by Dr. R. F. Bacon of this Bureau.[9]

Only two soda digestions on dita wood were made. The wood is very easily reduced, but its yields are 5 to 10 per cent lower than those of the others under identical conditions of treatment.

*Experiment 1.*—Strength of liquor, 4.4 per cent; 20 per cent caustic soda used calculated on the air-dried weight of the wood; pressure, 5 to 6 atmospheres; time, 8 hours; yield, 35 per cent.

*Experiment 2.*—Strength of liquor, 3.3 per cent; 15 per cent caustic soda used calculated on the weight of the wood; pressure, 5 to 6 atmospheres; time, 8 hours; yield, 38 per cent.

## SULPHITE WOOD PULP.

I have conducted a large number of sulphite digestions on selected species of Philippine woods, under varying conditions of strength of liquor, duration of boiling, temperature and pressure. An upright, steel digester capable of holding several pounds of raw material was constructed for these experiments. The conditions obtained in practice were thus closely approximated and they furnish reliable data which can readily be calculated in terms of ton lots of raw materials and of chemicals.

Considerable difficulty was encountered in constructing a gas-tight digester and in protecting the iron shell from the corrosive action of sulphite liquors. After failing in several attempts to make sheet-lead or silicate-paint linings which would hold, the following arrangement suggested by the Director was adopted throughout all the sulphite experiments.

A large stoneware chemical jar with ground stone cap and spring clip seal was placed inside the steel digester shell and surrounded with water containing sufficient alkaline bicarbonate to equalize the pressure produced by the free sulphurous acid gas on the inside of the jar. A drop tube carrying a thermometer and dipping into the outside liquor between the stone and iron walls allowed of perfect registration of the temperature conditions of the digestions.

In a small way, we were able to deposit a very smooth adherent lead lining on iron by the Bett's[10] process for refining base bullion in fluosilicic acid solution, but the proper current density and other conditions were not at hand for lining our large digester in this manner.

The woods were barked and chipped in the usual manner and cooked by the quick-cook system, namely at high temperatures for a relatively short time.

[9] *This Journal* (1906), 1, 1007.

[10] *Electro Chem. and Metallurgical Ind.* (1905) 3, 272.

TABLE No. 8.—*Sulphite digestions on Philippine woods (quick-cooking process).*

| Kind of wood and experiment No. | Composition of liquor. | | | Duration of digestion. | | Maximum temperature carried. | Yield of pulp. | | Bleaching powder consumed. | Screenings. |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total $SO_2$. | Combined $SO_2$. | Available $SO_2$. | Time to reach maximum temperature. | Total time. | | Unbleached. | Bleached. | | |
| Lauan: | *Per cent.* | *Per cent.* | *Per cent.* | *Hours.* | *Hours.* | °C. | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 3.6 | 1.6 | 2.0 | 4 | 12 | 160 | 42.2 | | | 1.8 |
| 2 | 3.5 | 1.2 | 2.3 | 5½ | 11 | 150 | 44.4 | 43.3 | 13.4 | |
| 3 | 3.75 | 1.78 | 1.97 | 4½ | 11 | 155 | 46 | | | 1.75 |
| Mayapis: | | | | | | | | | | |
| 1 | 3.52 | 1.63 | 1.89 | 4½ | 9 | 154 | 47.27 | | | |
| 2 | 3.45 | 1.35 | 2.10 | 5½ | 11 | 150 | 44.75 | 42.35 | 14 | |
| 3 | 3.75 | 1.78 | 1.97 | 4½ | 11 | 155 | 46 | | | 1.4 |
| Cupang: | | | | | | | | | | |
| 1 | 3.6 | 1.2 | 2.4 | 4 | 10 | 145–155 | 46.76 | 43.02 | 8.51 | |
| 2 | 3 | | | 4 | 16 | 160 | 49.4 | | | 3.0 |
| 3 | 3.75 | 1.78 | 1.97 | 4½ | 11 | 155 | 47 | | | 0 |

The following conclusion are drawn from the experimental data which have been tabulated and from the general appearance and feel of the resulting pulps:

A certain excess of sulphurous acid over the amount necessary to form the bisulphite of the base is desirable, first, because it tends to prevent the formation and separation of the monosulphite of calcium, which is extremely hard to wash out and which is liable to cause specks throughout the pulp; second, it is a more economical liquor to prepare. However, too great an excess of free acid is sure to produce a brown pulp similar to those resulting when sulphurous acid is used alone without any base being present. The liquor should contain about twice as much available acid—that is, acid combined as the bisulphite of the base and acid absolutely free, as is combined in the form of the mono or normal sulphite. Such a liquor will allow of digestions at the maximum temperature of 160° and at even higher ones, without danger of burning the chips if no gas is blown off during the cooking operation. A liquor of this composition will complete the cook in from ten to twelve hours if the charges have previously been thoroughly steamed and four hours are consumed in reaching the maximum temperature ultimately carried.

*Remarks.*—The sulphite digestions were regulated entirely by the temperature and no gas was blown off at any time. The chips were invariably steamed before the sulphite liquor was run in, and just sufficient liquor barely to cover the well-tamped charge was used. A heavy, perforated lead disc placed on top of the wood kept all the chips submerged. No device to induce circulation of the liquor during the boiling

was employed. The heat was applied by direct flame and the charge was always left in the digester after the completion of the cook until the following morning. The chips of all the experiments reported in the above table were of a light, salmon color when discharged, and the liquor was a clear brown and still contained free sulphurous acid. The pulp washed and beat easily to nearly white, soft fiber. Analyses of the unbleached fibers given in Table No. 9, page 93, serve to indicate the extent to which the incrusting matters were removed, under the corresponding digestion conditions.

### SULPHITE PULP FROM FIBERS OTHER THAN WOOD.

Within recent years numerous attempts have been made to apply the bisulphite or acid treatment to the manufacture of cellulose from the cereal straws; this was pointed out in a previous paper [11] but the siliceous nature of straw has heretofore stood in the way of a satisfactory isolation of the cellulose by this method.

Dietz[12] proposes first to remove the greater proportion of the ash content of the straw before submitting it to the action of the sulphite liquor. He has shown that a preliminary treatment with the theoretical quantity of hydrofluoric acid, calculated on the basis of the silica content of the straw, in the form of a 0.5 to 1.25 per cent solution, is capable of reducing the 1.5 to 3.7 per cent of silica normally present to less than 0.05. After such treatment, the straw is said to be quite suitable for digestion with bisulphite liquors. The best conditions for boiling the straw thus purified are given by an ordinary calcium bisulphite liquor containing 3.6 per cent total sulphurous acid, of which 2.4 per cent is free and 1.2 per cent combined. The boiling should be regulated so that a pressure of 3.5 atmospheres is reached in an hour and maintained for three hours. By this procedure the author obtained a 42 per cent yield of pulp which bleached well with 13 per cent of bleaching powder. Whether the partial removal of the silica in this manner will prove to be economically practicable remains to be seen. The increased yield of straw cellulose and the short time required to produce it, should be considered to be very attractive on the continent, where this material is quite highly prized for paper stock. In view of some results to be described later, obtained in pulping bamboo by means of sulphurous acid, I do not believe it to be necessary partially to remove the mineral constituents from highly silicated materials, before their treatment with sulphite liquors.

Other raw materials besides the Philippine woods already described, from which sulphite pulp has been prepared in this laboratory are hemp waste, old rope, jute gunny sacks and dwarf bamboo. The experiments

[11] *This Journal* (1906), **1**, 437.
[12] *Ztschr. f. angew. Chemie.* (1905), **28**, 648.

were conducted with the view of determining the exact conditions conducive of the best results in yield, color, ease of bleaching and strength of the resulting pulps; the conditions of the digestions; namely, strength of liquor, proportion of free and combined acid, proportion of liquor to material digested, temperatures employed and duration of the cooking are given below.

SULPHITE BAMBOO PULP.

*Preparation.*—Mature and seasoned culms of dwarf bamboo were crushed between rollers and chopped into 3 to 4 inch lengths. Some charges were thoroughly steamed before the sulphite liquor was added and in others the liquor was run in upon the dry chips. Bamboo prepared in the above manner forms dense, flat pieces which lie very close together and which allow of being covered with considerably less liquor than an equivalent weight of chipped wood. In all the digestions the weight of the bamboo to the weight of the liquor used was $\frac{1}{3.5}$ to $\frac{1}{4}$—that is, 15.12 liters (four gallons) of liquor was the maximum amount employed in any case for 4.5+ kilos (10 pounds) of bamboo chips.

*Experiment 1.*—Unsteamed chips were gradually heated through a period of four hours to a maximum temperature of 150° C. and maintained at this point for four hours longer, giving eight hours for the entire digestion. The charge was blown out under pressure; the chips were light, salmon-colored and apparently digested. The yield of air-dry pulp was 56.6 per cent. The liquor carried 3.5 per cent of sulphurous acid, all combined as the bisulphite.

*Experiment 2.*—Five kilos of well-steamed bamboo were covered with 13.23 liters (3.5 gallons) of bisulphite liquor, containing 3.45 per cent of total sulphurous acid, and heated up directly to a maximum of 155°, this temperature being maintained for a total period of ten hours. The chips were soft, light-brown in color, and they bleached with difficulty. The yield of unbleached pulp was 51.7 per cent; the yield of bleached was 48.4 per cent, with a consumption of 22 per cent of bleaching powder of 35 per cent available chlorine.

*Experiment 3.*—Two and one-half kilos (5.5 pounds) each of steamed bamboo and cupang wood were digested with 15.12 liters (4 gallons) of liquor of the following composition:

| | Per cent. |
|---|---|
| German method: | |
| Total sulphurous acid | 3.6 |
| Free sulphurous acid | 2.4 |
| Sulphurous acid combined as monosulphite of calcium | 1.2 |
| Lime, CaO | 1.05 |
| American method: | |
| Total sulphurous acid | 3.6 |
| Free sulphurous acid | 1.2 |
| Sulphurous acid combined as bisulphite of calcium | 2.4 |
| Lime, CaO | 1.05 |

The cook was heated up to 155° in four hours and maintained at 145° to 155° C. for a total period of ten hours. The yield of cellulose from the cupang was 46.76 per cent, from the bamboo 47.32 per cent.

Both the cupang and the bamboo fibers were of good appearance throughout, soft and nearly as white as bleached pulp. The bamboo pulp consumed 16.8 per cent of bleaching powder in two treatments; the yield of pure, bleached cellulose being 45.3 per cent. See Table No. 8 for the bleach consumption and yield of bleached cupang fiber. Analyses of both pulps in the unbleached state are given in Table No. 9.

TABLE No. 9.—*Analyses of unbleached sulphite fibers prepared by the quick-cooking process.*

| | Moisture (loss at 100° C.). | Resins (solution in alcohol). | Hydrocellulose solution in 1 per cent alkali. | Cellulose. | Non-cellulose (legrin) by difference. | Mineral matter (ash). |
|---|---|---|---|---|---|---|
| | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| Lauan | 9.20 | 0.91 | 5.77 | 81.42 | 2.19 | 0.51 |
| Mayapis | 8.88 | .63 | 6.29 | 80.57 | 3.31 | .32 |
| Cupang | 8.99 | .50 | 4.16 | 82.60 | 3.04 | .71 |
| Dwarf bamboo | 9.08 | | 9.04 | 72.36 | 4.37 | 5.15 |
| | 8.57 | | 6.94 | 78.68 | 3.67 | 2.14 |
| Jute (old bagging) | 8.07 | | 8.93 | 79 | 3.47 | .53 |
| Manila hemp (old rope) | 8.03 | | 12.02 | 77.40 | 1.95 | .60 |
| Spruce[a] | 6.13–6.70 | | 1.52–4.25 | 81.31–89.74 | .73–9.37 | .33–1 |

[a] The figures for sulphite spruce fiber are the extremes found by Griffin and Little on analysis of four samples of unbleached pulp prepared by the quick-cook process.

MANILA HEMP—OLD ROPE.

Very dirty, 3-inch cable rope cut down and well cleaned and dusted by hand, lost 21 per cent in weight.

*Experiment 1.*—Digested with a straight bisulphite liquor containing 3.54 per cent total sulphurous acid. A temperature of 140° C. was reached in two hours and held at 140° to 145° C. for four hours more. The fiber was nearly white, clean and strong; the yield of air-dry, unbleached pulp was 72 per cent, calculated on the cleaned material, and 56.88 per cent calculated on the original weight of the rope.

*Experiment 2.*—3.75 kilos (7.5 pounds) of rope prepared as above and 1.25 kilos (2.5 pounds) of new jute bagging were digested with 15.12 liters (4 gallons) of calcium bisulphite liquor of 3.5 per cent total sulphurous acid content. A maximum temperature of 145° C. was reached in less than two hours and maintained for a total period of six hours. The pulp was clean, grayish and long fibered.

The yield unbleached was as follows: Rope, 71.5 per cent; jute, 62.6 per cent.

*Experiment 3.*—3.75 kilos (7.5 pounds) of rope of good quality which lost approximately 10 per cent in cleaning and 1.25 kilos (2.5 pounds) of very old jute bagging were digested with a bisulphite liquor of the following composition:

| | Per cent. |
|---|---|
| Total sulphurous acid | 3.55 |
| Sulphurous acid combined as monosulphite | 1.365 |
| Available acid | 1.185 |

A maximum temperature of 150° was reached in one hour and maintained for three hours—a total of four hours for the entire cook.

The yield was as follows: Rope fiber, 66.5 per cent; jute fiber, 56 per cent.

The chief features of the sulphite pulps made from Manila and jute stock are the light, gray color to be obtained direct from the washing engine.

ABACA WASTE—SULPHITE DIGESTIONS.

Baled waste from hand-stripped Manila hemp from Albay Province was thoroughly hand sorted and dusted to free it from coarse husks and sand; at least 50 per cent of the original weight of the waste being removed by this treatment. It was then cut to a suitable fineness (about 4 to 5 inch lengths) and closely packed into the digester, strong pressure being used to hold the charge submerged in a small volume of liquor. Four to five times its weight of liquor proved sufficient to pulp the material under the conditions of the respective experiments outlined below.

TABLE No. 10.—*Sulphite digestion of abaca waste.*

| Experiment No. | Composition of the liquor. | | | Duration of digestion. | | Maximum temperature carried. | Yield of unbleached pulp. |
|---|---|---|---|---|---|---|---|
| | Total $SO_2$. | Combined $SO_2$. | Available $SO_2$. | Time to reach maximum temperature. | Total time. | | |
| | *Per cent.* | *Per cent.* | *Per cent.* | *Hours.* | *Hours.* | °*C.* | *Per cent.* |
| 1 | 3.57 | 1.76 | 1.81 | 2 | 7 | 150 | 48.9 |
| 2 | 3.34 | 1.30 | 2.04 | 2 | 5 | 140–145 | 47 |
| 3[a] | 3.40 | 1.50 | 1.90 | 1½ | 6 | 145 | 48.75 |
| 4 | 3.6 | 1.2 | 2.40 | 2 | 5 | 150 | 50.76 |
| 5[a] | 3.55 | 1.36 | 2.18 | 1 | 4 | 140 | 59.2 |

[a] The charges for experiments 3 and 5 consisted of 8 pounds of hemp waste and 1 pound of jute bagging.

*Remarks.*—An ordinary bisulphite of lime and magnesia liquor, such as is generally used in the manufacture of sulphite wood pulp, is applicable to this material.

The state of subdivision and the extremely porous nature of the waste, allows of the heating of the boiler to the maximum temperature it is desired to maintain in the shortest possible time, without danger of burning the pulp.

Three to four hours' digestion at temperatures ranging between 140° and 150° C. will produce a strong, gray-colored stock which washes and beats readily by the usual methods, but these conditions of time and temperature do not dissolve all of the chaff and cellular matter present, and the result is a rather poor appearance when the pulps are molded into boards or sheets. The cellular matter remaining in the pulps is nonfibrous and has no felting power, but it does possess a cementing nature which adds to the strength of paper made from such half-stuff and I do not think that it will be necessary to attempt to remove all of the nonfibrous portions from hemp waste for the production of colored

or coated papers such as are used in the manufacture of heavy bags which are filled but once and where strength is the important characteristic desired.

The bale of waste upon which the above experiments were made is not considered to be as clean and well sorted as it is possible to obtain this material in practice, in fact I am informed that a much better grade is now being collected and baled in considerable quantities in the provinces.

An average yield of approximately 50 per cent of strong-fibered stock was obtained in the sulphite digestions outlined above, and this is about what may be expected from the best grades of waste it is possible to obtain, if the baled stuff is thoroughly deviled before it is subjected to any kind of chemical treatment.

*General conclusions.*—First. It is essential that the material should be clean and as free from foreign matter as mechanical cleaning processes will make it.

Second. A preliminary steaming of the charge in the boiler before the sulphite liquor is run in is advantageous mainly because it allows the material to be tamped down and covered with a much smaller quantity of liquor. Most of the materials treated are very bukly in the dry state and sufficient liquor to cover is greatly in excess of the amount necessary to do the work. The running in of cold water and allowing it to discharge answers the purpose.

Third. Because of the finely divided and porous nature of such materials, no gradual rise of temperature up to the maximum to be carried is necessary, as is true in treating dense, wood chips, but the digester may be heated up to full pressure at once, thus saving three to four hours in time.

Fourth. The stock is more easily washed and its color, as it appears when it is taken direct from the washing engines, is fully as light as the partially bleached lime or soda pulps made from this class of fibers, and this fact should be strongly emphasized not only because of saving in cost and of the time of a bleaching operation, but also because lignified fibers such as hemp, jute, etc., are very susceptible to chlorination during bleaching, and this seriously impairs the strength of the resulting stock.

I am not aware that sulphite jute or rope stock have ever been made commercially, but I see no reason why such stock would not be superior to that made by the old process, particularly as this class of fibers is invariably used in the manufacture of low-white or coated products, in which strength is the most important consideration. Mills running on jute, rope, straw, etc., will readily see the advantage of employing a process which cooks and bleaches a fiber in one operation, thus eliminating the losses of fiber and time incident to extra handling and excluding the solvent action on the fiber which alkaline liquors are known to possess, as well as the liability to deterioration in strength caused by poorly conducted bleaching.

## COMPARISON OF THE ACID AND ALKALINE PROCESSES OF PULP MANUFACTURE.

Some of the points of superiority claimed for the acid or bisulphite method of treatment are: greater yields, stronger fibers and greater economy in the cost of chemicals consumed. The adherents of the older, or alkaline method of treatment claim applicability to a wider range of raw materials, greater ease of manipulation and economy in cost of chemicals and time. There is no doubt but that greater yields and stronger stock are obtained by the bisulphite process, for as it is strictly a hydrolytic chemical reaction performed in a reducing atmosphere, the possibilities of oxidation are excluded, and therefore no loss of cellulose or weakening of the fiber results from this cause.

White pine wood, which is pulped by both processes, invariably in commercial practice yields about 10 per cent more sulphite than soda cellulose. Sulphite cellulose, in the common practice of blending different pulps to produce papers of certain qualities required by the trade, is relied upon for the property which it possesses of giving strength to the materials.

That alkaline solutions exert a solvent action on vegetable fibers is well known. Taus[13] in a series of carefully conducted experiments has shown that purified cotton cellulose is attacked by alkalies at the high temperatures and concentrations frequently employed for isolating paper cellulose by the soda process, and assuming that a soft wood (pine wood) contains 54 per cent of cellulose and 46 per cent of other matter, the latter or 46 per cent will be dissolved after three hours of digestion with 3 per cent caustic soda solution at a pressure of five to six atmospheres, but 70 per cent of the total cellulose and other matter would be dissolved with the same strength of liquor in the same period if the digestion were to be carried on at ten atmospheres, and approximately the same solvent action is effected if the time (three hours) and the pressure (five atmospheres) remain unchanged, but the strength of the alkaline liquor increased to 8 per cent. Now 8 per cent (12° Baumé) liquor is the rule rather than the exception in the actual practice of soda wood pulp production, and for the purpose of facilitating the mechanical loosening of the fibers and of effecting solution of the noncellular incrusting matters in the shortest possible time, pressures which are more nearly ten than five atmospheres are also adopted. In my opinion more thorough and better methods of preliminary preparation of woody tissue or of other raw cellular materials will accomplish the same purpose with an improvement both in quantity and quality of the resulting product. In all the experiments I have recorded on both soda and sulphite digestion of wood, the method of preparation—that is, the barking and chipping which are employed in

[13] *Dingler's Polyt. Journ.* (1890), **276**, 411–428.

actual practice—was followed, but repeated trials on wood in various states of subdivision conclusively showed that it was possible to produce an equivalent yield with a considerably weaker liquor in the same time, by doubling the number of chips per given weight. While there undoubtedly is a minimum limit beyond which wood could not safely be divided without impairing the length and strength of the fibers, that limit is by no means reached in present practice. Even the passing of the green, chipped wood under heavy crushing rollers, a procedure worked in some sulphite mills, is a very efficient means of mechanical disintegration.

The method of preparing wood for sulphite digestion and the improvements in the operation itself have resulted in a great saving of the time required for the digestions. It was usual, when the process was first applied, to boil the pulp for twenty hours or more, but now fourteen to sixteen hours, dependent upon the kind of wood and the quality of the pulp desired, is the more common practice.

Much has been written regarding the relative cost of the two processes of manufacture under discussion. Many factors enter into a calculation of the comparative cost of producing soda and sulphite cellulose. However, the problem is an important one in the event of the introduction of the industry in a new country and therefore it deserves some consideration. Leaving out the initial expense of installation, which is undoubtedly greater for a sulphite than for a soda plant, it is proposed briefly to discuss the relative cost of producing a ton of sulphite and soda pulp from white lauan or mayapis wood, the local market quotations on the chemicals required alone being considered.

Calculations for the production of 1 ton of sulphite pulp, based on the use of a straight bisulphite of calcium liquor of 3.5 per cent total sulphurous acid content and 1 per cent of lime, Japanese sulphur and native lime being used, are as follows:

Fifteen per cent of sulphur recovered; 2 cords of wood give 1 ton (2,000 pounds) of pulp; 8,399.16 liters (2,222 gallons) of liquor contain 295.3 kilograms (650 pounds) sulphurous acid, or 155.4 kilograms (341.88 pounds) of sulphur.[14]

| | |
|---|---|
| Sulphur is calculated at 2.75 cents per kilogram (1.25 cents per pound) | $4.27 |
| And 84.08 kilograms (185 pounds) lime, at 1.1 cents per kilogram (0.5 cent per pound) | .92 |
| | 5.19 |
| 15 per cent of sulphur recovered—that is, 23.33 kilos (51½ pounds)—at 2.75 cents per kilo (1.25 cents per pound) | .64 |
| | 4.55 |

[14] Ninety-five per cent of the sulphur burned being rendered available in the form of sulphur dioxide.

The calculations for the production of 1 ton (2,000 pounds) of soda pulp are based on the use of caustic soda made from imported soda ash and native lime. They are as follows:

7,560 liters (2,000 gallons) of caustic liquor of a specific gravity of 1.06 (8° Baumé, 5.25 per cent of caustic soda) contains approximately 400 kilograms (880 pounds) of alkali, which in turn requires for its manufacture:

| | |
|---|---|
| 300 kilos (660 pounds) lime, at 0.22 cent per kilo (0.5 cent per pound) | $3.30 |
| 534 kilos (1,176 pounds) soda ash, at 0.4 cent per kilo (1 cent per pound) | 11.76 |
| | 15.06 |
| 75 per cent of soda ash recovered as such, 400 kilos (882 pounds), at 0.4 cent per kilo (1 cent per pound) | 8.82 |
| | 6.24 |

While the above estimates are but rough approximations, they are to be considered as fairly conservative and they serve to indicate the cost of the crude chemicals actually consumed in the production of one ton of sulphite and soda pulp respectively. It will be noted that estimates for the sulphite liquor call for a consumption of 8,399 liters (2,222 gallons) for 2 cords of chips. In our sulphite digestions we were able to cover 4.54 kilos (10 pounds) of well-packed chips, previously steamed, with 18.90 liters (5 gallons) of liquor; this is equivalent to the above volume for 2 cords of the wood. However, in practice 9,450 liters (2,500 gallons) of liquor are usually employed. The sulphite liquor in the estimate and the one which was found to produce the best results in our experiments had the following composition:

| | Per cent. |
|---|---|
| Total sulphurous acid | 3.5 |
| Sulphurous acid combined, bisulphite of calcium | 2.28 |
| Sulphurous acid free (in excess of the amount necessary to form calcium bisulphite | 1.22 |
| Lime | 1.00 |

In Germany, all acid in excess of that which is necessary to form the monosulphite of calcium ($CaSO_3$) is termed free acid; hence according to the German system of nomenclature, the above liquor would contain:

| | Per cent. |
|---|---|
| Combined acid | 1.14 |
| Free or available acid | 2.36 |
| Total acid | 3.50 |

PULP- AND PAPER-MAKING CHEMICALS.

The following chemicals, *lime, sulphur, caustic soda, soda ash, chloride of lime, kaolin, talc, gypsum, alum,* etc., are largely consumed in the manufacture of paper pulp, their use being dependent upon the chemical process adopted for the conversion of raw fibrous material into paper stock and the particular grades of the finished product it is desired to make.

LIME.—Calcium oxide (CaO), commercially known as quick or caustic lime, is undoubtedly the most universally used reagent in the preparation of chemical pulp. Its source is the limestone deposits so widely distributed throughout the world. In the alkaline process of digestion, lime finds extensive use, either as such or in combination with soda ash for the preparation of caustic soda, when a more active alkaline reagent is required.

In the acid or bisulphite method of treatment, lime is the base most generally employed in the preparation of the sulphite liquors, here again it may either be used alone to form unmixed bisulphite of calcium liquors, or in conjunction with magnesia derived from the magnesian limestone, called dolomite.

A further use for lime in the paper industry is in the manufacture of bleaching powder (chloride of lime) and it may be employed in the form of the sulphate, as pearl hardening or as gypsum to furnish a mineral loading material in certain grades of paper.

SULPHUR.—The principal sources of the world's supply of sulphur are found in Sicily, in Louisiana and Utah in the United States, and in Japan. In the form in which it is brought on the market it is classified according to its degree of fineness. A second or third grade, containing one-half to one per cent of foreign matter and ash, is usually employed in the preparation of sulphite liquors. Sulphur comes to the mills in sacks or barrels and it is burned as needed, the sulphurous acid gas which is formed either being passed into water containing the lime in solution or suspension, or through a long vertical column of coarse limestone or dolomite, sprinkled with water.

CAUSTIC SODA AND SODA ASH.—Caustic soda (NaOH) and soda ash ($Na_2CO_3$) appear on the market in different states of purity, their value depending on the amount of alkali ($Na_2O$) present. The grades which find most general use among paper makers are 78 per cent caustic soda and 48 per cent ash.

The present market quotations are as follows:[15]

| | |
|---|---|
| Caustic soda (78 per cent), per cwt | $1.75–1.85 |
| Soda ash (48 per cent), per cwt | .75– .80 |

[15] The duty on these chemicals on entering the port of Manila is 25 cents per 100 kilos (220 pounds) gross weight. (Philippine Customs Tariff, Par. 93.)

Bleaching powder (chloride of lime) is valued on its content of available chlorine; it is somewhat unstable and it readily deteriorates in strength on exposure to heat, air and moisture. When freshly prepared it contains about 40 per cent of available chlorine. Analyses of several samples of bleaching powder purchased in the Manila market have shown a strength of less than 30 per cent in every instance. In view of this loss which bleaching powder undergoes during long periods of transit, it is questionable whether it would not be more economical to import the liquid chlorine and manufacture bleaching powder here as needed.

The older method of gas bleaching, making use of chlorine in the gaseous form, was displaced by the use of chlorine in combination with lime because of the simplicity and ease of control of the operation with the latter, but with bleaching powder at $1.25 per hundredweight and because of its arrival in Manila at a point nearer 20 than 30 per cent in strength, it could not compete with liquid chlorine at its present market quotations.

About one-half of the world's output of bleaching powder is prepared from chlorine made by electrolyzing crude salt. Crude salt from sea-water evaporation is both cheap and plentiful.

Mineral fillers.—Nearly all kinds of paper contain varying amounts of some form of mineral matter. These are added to the pulp in the beating engines for the purpose of increasing the weight, filling up the pores and imparting a better feel and appearance to the finished sheet. The substances best suited for these purposes are certain grades of clay, sulphate of calcium, talc, gypsum, barytes, etc. They should be of light specific gravity, free from grit and should be white, showing a low content of iron and organic impurities.

The Mining Division of the Bureau of Science submits the following data concerning the local supply of crude chemicals, their cost and availability:

Limestone.—The sources of supply of burned lime for Manila are (*a*) the limestone quarries near Binangonan on Laguna de Bay in Rizal Province and (*b*) a coral limestone from marine shells burned near Malabon on Manila Bay.

(*a*) The quarries at Binangonan have a present annual output of about 600 tons, mostly of water-slaked lime which is sold in Manila for making mortar. This lime can be obtained fresh burned when it is needed, as is the general custom throughout the Archipelago. The product is a very fat lime, which swells when it is slaked to about three times its original volume. The lime is valued at Binangonan in proportion to its content of calcium oxide. The present prices are as follows:

| | |
|---|---|
| Quick lime, per cavan (about 80 pounds) | ₱1.35 |
| Slaked lime, per cavan (about 80 pounds) | .45 |

The transportation charges from Binangonan to Manila are ₱0.15 per cavan, which make the prices in Manila ₱1.50 and ₱0.60 per cavan for

the quick and slaked lime, respectively. As there is a profit in this of about ₱0.60 per cavan for quick lime and ₱0.17 for slaked lime, it will be seen that if the consumer were to burn his own lime, under present conditions it would cost about ₱0.90 per cavan of 80 pounds in Manila. This is one cent Philippine currency or one-half cent United States currency per pound. This rate is excessive, but it is obtained under conditions of manufacture and transportation which are of the crudest description. With a modern plant, running under favorable conditions as regards quarrying, fuel and labor, I can see no reason why quick lime should cost more that one-half of this figure.

(*b*) At Malabon about 600 tons of slaked lime are also produced annually. This, like other lime obtained along the shores of marine waters, is derived from coral. It is produced at Malabon for ₱0.25 per cavan, and it costs ₱0.38 per cavan in Manila. The greater part of it is used for mortar and whitewash. Other points near Manila where lime is being burned are Malolos, Angat and Baliuag in Bulacan Province and at Sexmoán and Guagua in Pampanga. In general, a limestone belt extends from Binangonan in Rizal Province north through Bulacan and into the Province of Nueva Ecija. The Cabanatuan branch of the Manila and Dagupan Railroad runs nearly parallel to it and through the towns where quarries are at present situated and it is firmly believed that a practically unlimited supply of good lime will readily be available for economic use when the occasion demands. Other localities upon which definite information is at hand concerning the extent of the deposits of limestone and their accessibility include the islands of Batan, Romblon, Cebu and Panay. The limestone deposits of Batan Island are particularly of interest from the standpoint of their use in the manufacture of paper, because of their proximity to the coal fields and also because of their location with respect to the most promising available supplies of raw material, namely the Manila hemp growing districts.

An exceptionally pure limestone is found in northern Panay, outcropping in large masses on both banks of the Badbaran River between Dumarao and Maabutang and also about 4 miles from the former place, which lies on the line of the proposed railroad from Iloilo to Capiz. Old lime-kilns used by the Spaniards for burning this stone are near by. This limestone is cream colored, compact and semi-crystalline, with a low iron and silica content. A large deposit of very pure limestone occurs near Pilar on the north coast of Panay, it is very similar in appearance to the other Panay limestone which has just been described, and it should prove well fitted for the manufacture of quick lime. It is situated in the center of a large mangrove forest from which any quantity of cheap fuel could be obtained, and being close to the sea the problem of transportation is minimized.

The following table gives the results of analyses of some Philippine limestones:

TABLE No. 11.—*Analyses of some Philippine limestones (calculated to calcined material).*

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Silica ($SiO_2$) | 1.06 | 2.19 | 0.49 | 1.55 | 0.89 | 2.49 | 0.37 | 0.57 | 1.15 | 0.62 | 0.01 |
| Iron ($Fe_2O_3$) | .29 | .24 | .38 | .82 | .39 | .90 | 1.25 | .26 | .67 | .84 | .29 |
| Lime (CaO) | 94.80 | 94.24 | 98.12 | 96.34 | 97.41 | 94.62 | 96.88 | 97.00 | 96.92 | 95.91 | 97.39 |
| Magnesia (MgO) | 1.96 | 2.44 | .98 | 1.27 | .48 | .21 | .72 | 1.40 | 1.24 | .51 | 2.39 |

NOTE.—Numbers 1 and 2 are from Anabang near Angat and from Santa Margarita Springs respectively, both in Bulacan Province, Luzon; 3 and 4 are from the quarries near Binangonan, Rizal Province, Luzon; 5 and 6, from Batan Island near Legaspi, Albay Province, Luzon; 7 and 8 are taken from near Dumarao and Pilar, Capiz Province, Panay; 9 is a coral limestone from Malabon on Manila Bay; 10, a suitable causticizing lime; 11, a suitable liquor-making lime.

LOADING MATERIALS.

*Kaolin.*—While but little prospecting work has been done on the clay deposits of the Philippines, there seems little doubt but that the supply which may be obtained is so extensive that the question of importing this crude chemical will never arise. A general inquiry concerning Philippine clay deposits for the purpose of establishing a school for pottery making has been begun by the Bureau of Education and a systematic study of the physical and chemical properties of various clays for different economic uses is under way in this Bureau at the present time. Below is given the chemical composition of some clays from Laguna Province and from the Island of Romblon:

TABLE No. 12.—*Chemical composition of some clays from Laguna Province and from the Island of Romblon.*

| | 1. | 2. | 3. | 4. | A. | B. | C. | D. |
|---|---|---|---|---|---|---|---|---|
| Moisture, loss at 100°–110° | 0.30 | 10.15 | 7.09 | 9.10 | 1.60 | 1.24 | 2.66 | 0.63 |
| Loss on ignition | 12.27 | 10.77 | 11.27 | 12.79 | 12.56 | 12.67 | 13.50 | 13.73 |
| Silica ($SiO_2$) | 47.56 | 42.77 | 43.50 | 41.16 | 44.30 | 45.24 | 44.15 | 47.76 |
| Aluminia ($Al_2O_3$) | 38.12 | 33.48 | 35.48 | 35.84 | 38.64 | 37.59 | 36.54 | 37.04 |
| Ferric oxide ($Fe_2O_3$) | 0.08 | 1.04 | Trace. | .67 | .83 | 1.00 | 1.04 | .75 |
| Lime (CaO) | .39 | 1.61 | .17 | .42 | .39 | .66 | .15 | .06 |
| Magnesia (MgO) | 0.0 | .16 | .41 | .02 | .42 | | | .14 |
| Alkalis ($Na_2O$, $K_2O$) | 1.28 | .11 | 2.08 | | 1.18 | 1.69 | .98 | .52 |
| Specific gravity | 2.8625 | 2.5585 | | | 2.5451 | 2.91 | | 2.46 |

NOTE.—Numbers 1, 2, 3, and 4 are taken from Griffin and Little,[16] as suitable clays for paper makers; A, B, and C are Philippine clays from Laguna Province; D is from Romblon.

[16] Chem. Paper Making: (1894) 316.

*Agalite, or ground talc,* as it is commonly termed, has come into extensive use as a mineral filler in paper manufacture. Like asbestos, it has a distinct fibrous structure which causes it to blend well with the vegetable fiber of the pulp and thus to be retained without the considerable loss incidental to the use of china clay or sulphate of lime for this purpose. The more valuable talc for paper loading consists of altered tremolite, the fibrous structure of which is largely retained. According to the statistics of the New York State Geological Survey for 1905, there were produced 67,000 short tons of fibrous talc, valued at $469,000, or an average of $7 per ton. Practically the entire output finds its way to the paper mills. Tremolite from Ilocos Norte, Luzon, was examined in the Division of Chemistry, Bureau of Science. It consisted of irregular, foliated masses of a beautiful greenish-white tint. Ground in a ball-mill and then passed through a sieve of 100 meshes it is a greenish-white impalpable powder with a very soapy feel. It appears as minute, elongated crystals or fibers when seen under the microscope. Its chemical composition, compared with that of a commercial talc, is as follows:

| | Water (loss on ignition). | Silica ($SiO_2$). | Alumina ($Al_2O_3$). | Ferric oxide ($Fe_2O_3$). | Lime (CaO). | Magnesia (MgO). | Specific gravity (Joly balance). |
|---|---|---|---|---|---|---|---|
| | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| Ilocos Norte altered tremolite | 2.33 | 57.62 | 1.66 | 1.36 | 13.38 | 24.18 | 2.84 |
| Agalite | 2.67 | 61.82 | 1.59 | | 3.65 | 29.98 | 2.6–2.8 |

The specimen which was examined, when judged by its physical properties, would be considered of very good quality for the purpose of the paper manufacturer. It is easily ground, is of good color and is especially free from grit.

No definite figures with respect to the extent of the deposit can be given. However, it has the advantage of being situated near the sea and development work should show large pockets of talc in connection with mica.

*Sulphur and pyrites.*—Although sulphur is found widely distributed throughout the Philippine Archipelago, careful search has failed to locate any deposits of commercial importance. The most favorable outlook for native sulphur is from near Barauen in Leyte and from the Island of Biliran, which, on superficial examination, show 3,000 and 400 tons of sulphur in sight, respectively, but both these deposits are too small to warrant the necessary cost of extraction and transportation.

*Pyrites.*—The only deposit of this mineral of any extent and so far reliably reported, is in Lepanto Province, and here again the question of transportation, for the present at least, throws it out of reckoning as a commercial possibility.

*Japanese sulphur.*—The nearest and no doubt cheapest source of a supply of sulphur for industrial use in the Philippines, is Japan. The output of the Japanese sulphur mines for 1904 was 20,000 tons. About three-fourths of the total product is exported, the United States of America and Australia being the chief consumers. Recent quotations are $17.50 a ton for the best grades and $15.50 for seconds and thirds. As the yield of sulphur from Japanese ore is probably the highest in the world, this cost will allow it to be laid down in Manila, duty prepaid, at a price but slightly if any in advance of the market quotations on American sulphur. The fact that Japanese sulphur enters the United States in competition with the home product bears out the above statement. Five samples of Japanese refined sulphurs submitted by the Mitsui Bussan Kaisha were found to assay from 99.3 to 99.82 per cent in extremes of fineness.

## FUEL.

Coal of a fairly uniform quality is found widely distributed throughout the Islands. The largest known deposits are located on the Islands of Batan, Cebu and Polillo, but it also occurs in greater or less quantities in Negros, Mindanao, Samar, Masbate, Mindoro, and in the Provinces of Rizal and Nueva Viscaya on Luzon.

Recent work [17] in this Bureau on the Philippine Coals has shown that they are of much better quality for steaming purposes than was hitherto supposed, and that the poorer grades are very satisfactory from the standpoint of producer gas manufacture.[18] For more detailed accounts of the distribution and fuel properties of Philippine coals, see The Coal Deposits of Batan Island [19] and The Coal Measures of the Philippines.[20]

*Wood for fuel* is both cheap and abundant in many localities. The principal source of firewood is found in the widely distributed mangrove swamps of the seacoast. The mangrove forests are composed of a number of trees which produce dye and tan barks for local use and in which there is some trade. Work on Philippine mangrove tan barks is in progress in this Bureau and it is believed that they will compare favorably with the similar species which are handled commercially in Africa, Borneo, Java and elsewhere. An exploitation of mangrove tan bark will materially increase the available supply of cheap fuel for lime burning and other industrial purposes.

*Oil for fuel.*—The possibility of the use of oil as fuel in the Philippines is as yet uncertain, although a small quantity of oil is known to exist in Tayabas Province, Luzon, and gas has been encountered in drilling artesian wells in Pampanga Province.

[17] Cox, A. J.: *This Journal* (1907) **11**, 41.
[18] Cox, A. J.: *Ibid.* (1906) **1**, 877.
[19] Smith, D. D.: *Phil. Mining Bureau Bul.* Manila (1905) No. 5.
[20] Burrett, C. H.: *U. S. War Dept., Div. Ins. Affairs, Bul.* (1901).

PAPER MILL WATER.

Large quantities of water are required in the manufacture of pulp and paper, and its quality is of the first importance. In no other industry making use of large quantities of water in the processes of manufacture, is the purity of the water more carefully guarded. A soft water is not demanded for making the liquors used in the boiling of stock, because it is necessarily rendered hard in the operation. For washing the pulp and for steam-making purposes a soft water is desirable and even necessary. The importance of using a very soft water in the other departments of paper manufacture is perhaps overestimated. It is of more concern that the water be clear and especially free from iron, sediment and organic matter. A factory making use of the waters of small streams will be troubled by turbidity during the rainy season of the year. A better source would be in wells or reservoirs fed by pure water brought by conduits from mountain streams. Artesian wells furnish the greater supply of water in use here at the present time for boilers and industrial purposes.

A series of fifty-two analyses of the Manila city water supply, extending over a period of seven months and representing portions of both the dry and rainy seasons gave the following extremes in parts per million:[21]

| | Maximum. | Minimum. |
|---|---|---|
| Total residue | 220 | 153 |
| Fixed residue | 190 | 127 |
| Volatile matter | 46 | 16 |
| Oxygen consumed | 2.20 | .65 |
| Chlorine | 4.40 | 2.13 |
| Hardness | 109 | 58.8 |

*Remarks.*—The above analyses[22] were made on unfiltered water and they show a high degree of purity. The oxygen consuming power, equivalent to bleach consuming power, is remarkably low. The source of this supply is the Mariquina River which empties into the Pasig River between Manila Bay and Lake Laguna.

The mineral constituents of a water affect its value for paper or pulp manufacture mainly as they bear upon its suitability for boiler purposes. Philippine ground and surface waters as a class are considered to be moderately hard.

While none of the boiler waters which were examined contain sulphate of calcium, some of them have a high silica content which forms a troublesome scale.

A table of analyses of boiler waters collected from various provinces and islands of the Archipelago is given on page 106.

[21] Parts per millon×0.058=grains per United States gallon.

[22] Bliss, C. L.; *Publications of the Bureau of Government Laboratories* (1904) No. 20.

TABLE No. 13.—*Analyses of some Philippine waters.*

[Parts per million, which multiplied by 0.0058 gives grams per United States gallon.]

| Laboratory No. | Total residue. | Volatile residue. | Fixed residue. | Nonscale-forming ingredients. | Scale-forming ingredients. | Silica, $SiO_2$. | $Fe_2O_3$ $Al_2O_3$. | CaO. | MgO. | $SO_3$. | Quality. | Source. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3545 | 2,248 | 1,081 | 1,167 | 807 | 360 | 43.3 | 17.6 | 195.2 | 142 | Trace | Moderately hard | |
| 3601 | 949 | 48 | 901 | 554 | 347 | 38.8 | Trace | 159.4 | 55 | 58 | Soft | Cebu. |
| 35025 | 483.5 | 118.5 | 365 | 178.8 | 186.2 | 30 | 4 | 62 | 26.5 | 28.46 | Hard | Jaro River, Jaro, Iloilo Province, Panay. |
| 37929 | 359.1 | 32.4 | 3,267 | 74.1 | 252.6 | 37.6 | 1.4 | 87.8 | 39.4 | 1.3 | Moderately hard | Cebu. |
| 5100 | 1,757 | 40.80 | 1,716.4 | 1,499.3 | 217.1 | 55 | .4 | 65.1 | 1.2 | 89.66 | Hard | Isla del Provisor, Manila. |
| 4673 | 2,583.8 | 68 | 2,515.8 | 2,381.4 | 134.4 | 27 | 10.80 | 53.8 | 29.2 | 2.74 | do | Artesian well, Quarantine Station, Cauit Island, Cebu. |
| 4001 | 1,499 | 25 | 1,474 | 1,398.5 | 75 | 41.75 | 1.50 | 11.25 | 12.61 | 92.34 | do | |
| 4503 | 1,629 | 52 | 1,577 | 1,481 | 96 | 37 | 2 | 13 | 19.47 | 4.12 | do | Cebu. |
| | 215.4 | | | | | 44.7 | 6.8 | 23 | 9 | 15.6 | | Manila water supply. |
| | 153 | 24 | 129 | | | | .25 | | | | | Pampanga River, near Calumpit, Luzon. |
| | 391.6 | 4.2 | 387.4 | 71.7 | 315.7 | 46.4 | .4 | 133 | 23.49 | 3.09 | | Cebu (terminal) R. R. |
| 37929 (*a*) | 389.7 | 5.2 | 384.5 | 94.1 | 290.4 | 24.5 | 1.3 | 128.7 | 17.1 | 3.3 | Hard | Cebu. |
| 37929 (*b*) | 348.5 | 21.5 | 327 | 86.7 | 240.3 | 22.9 | 1.5 | 97.8 | 12.8 | 7 | do | Do. |
| 37929 (*c*) | 359.1 | 32.4 | 326.7 | 74.1 | 252.6 | 37.6 | 1.4 | 87.8 | 39.4 | 1.3 | do | Do. |
| 35024 | 348.1 | 141.5 | 406.6 | 157.8 | 248.8 | 56.6 | 4 | 65.2 | 28.19 | 38.06 | | Jaro River at Lapaz, Iloilo Province, Panay. |

### WATER POWER.

Abundance of water power in the past has been a more important factor in determining the location of paper mills than the nearness to the source of raw materials or to the market. At the present time this applies more particularly to plants producing mechanical or ground wood pulp. Steam is necessary for the manufacture of chemical pulp as it is used for heating the digesters and it also furnishes a much more efficient and easily controlled power for running paper mill machinery. There is an abundance of water power in the Philippines, but the cost of installing plants and their location with respect to the commercial centers precludes its utilization at the present time.

### MARKETS.

*The market in the Philippines.*—The first consideration of the new industry would manifestly be to supply the home market with those grades of paper for which the raw materials are best suited. The annual imports of paper of all kinds into the Philippine Islands approximates $1,000,000 in value and the demand for newspapers, magazines and books is multiplying yearly. This increased demand is but the natural result of the growth of the public school system throughout the Islands, which creates a greater desire for the knowledge of Western countries. The main items of the total importation are pulp, writing, printing and wrapping papers, all of which could largely be produced from native raw materials. The local supply of cotton and linen rags could be drawn upon for the finer grades of writing and note paper. No other city of its size in the world is so large a consumer of cotton and linen textiles as Manila. For the greater part, these are bleached and unadulterated with woolen fiber, so that the very best grade of paper rags could no doubt be collected here in considerable quantities.

*The foreign market.*—Japan is a large importer of paper, approximately $2,750,000 in value having been brought into that country in 1905. Japanese paper is principally made from rice straw and from the bark of the mulberry, but the demand for wood pulp has increased so greatly in the last four or five years that the Japanese Government has begun a systematic study of the suitability of Japanese timber for the purpose of manufacturing this article.

In China, the trade in paper has also attained considerable dimensions, statistics for 1905 showing importations approximating $2,000,000 in value. Foreign capital has recently entered the field for the purpose of manufacturing paper from bamboo, rice straw, etc., so as to meet the rapidly growing trade. The nearness of both the Chinese and Japanese markets should enable Philippine manufacturers to obtain at least a share of the trade in this commodity.

## FURTHER OBSERVATIONS ON THE DISTRIBUTION AND AVAILABILITY OF THE RAW MATERIALS WHICH WERE DISCUSSED IN THE ENTIRE SERIES OF ARTICLES ON THIS SUBJECT.

### MANILA HEMP (ABACÁ) WASTE.

A considerable quantity of Manila hemp waste has been exported from the Islands since my work on the suitability of this material for paper making was published; thus the problems incident to its collection, curing, sorting, baling and transportation are being solved by the commercial interests involved. It remains to be seen whether the costs of baling and transporting large quantities of waste from the abacá growing districts to Manila and thence to New York or London will allow of this material being economically exported. Fundamentally, it is contrary to commercial practice to attempt to export such a cheap and bulky commodity for long distances, particularly when only about 40 per cent of a given weight is of any value for the purpose for which it is intended. It is self-evident that if this raw material were pulped on or near the place where it is produced, the reduction in the cost of baling and shipping would allow a more attractive price to be paid for the material itself, and better methods of curing and sorting could be inaugurated.

In my opinion the reduction in cost of freight and handling incident to placing abacá waste half-stuff on a foreign market, thus allowing a greater outlay in properly preparing the waste for the digestion process, is certain to bring better results if the quality of the resulting product alone is considered, than would the exportation of the raw product. To pulp the waste here for subsequent exportation would effect a reduction of 50 per cent in freights alone. The initial cost and daily running expenses of an hydraulic baling press would nearly offset the cost of equipment for a pulp mill of 10 tons daily capacity.

### COGON GRASS.[23]

*Distribution.*—The following data with reference to cogon grass are taken from a report of observations on paper materials in Tarlac made by myself while traveling over that province in December, 1906. Cogon of good quality is found between Capas and Concepcion, Tarlac Province, Luzon; the country is level, consisting for the most part of deserted rice and sugar lands which contain some scattering scrub timber. A good road of 7 miles, with but one ford, connects the two places. The two grasses, cogon and talâhib, are almost invariably found together, the predominance of one over the other depending upon the altitude, the talâhib being more plentiful in low places. At this season of the year talâhib has flowered and is rapidly drying and becoming worthless.

[23] See Richmond, Geo. F.: *This Journal* (1906), 1, for the discussion of cogon and talâhib as materials for paper making.

Cogon being partially protected from the sun by the taller taláhib is more green and thrifty.

From Capas to O'Donnell the road runs 10 miles to the west, slightly up grade but fairly level; the region is entirely uncultivated; it is too high for rice and too poor for sugar; much grass grows everywhere, but it is of an inferior grade, due to lateness of the season.

There is a good bull-cart road for about 7 miles east from the town of Tarlac in the direction of La Paz; the country is level, the first 3 miles being under cultivation in rice; a mile of quite dense woodland occurs and then 3 miles of uncultivated country follows, covered with a good quality of grass. The country is more rolling and hilly from Tarlac westward in the direction of Moriones, with grass everywhere, pure in the valleys but contaminated with buffalo grass on the hills. The natives informed me that cogon, called *ilib* in Pampanga, is not eaten by horses and cattle, but that they do forage on the young shoots of taláhib.

Practically all the houses in Tarlac Province, with the exception of those in the towns on the railroad, are constructed of cogon. Taláhib is scarcely ever used for this purpose, but the latter finds some employment in the construction of fences for yard and garden inclosures. I observed large stacks of cogon in the various barrios. The natives know when and how to harvest this grass, having learned this because nipa is too expensive for general use as a roofing material in all localities distant from the tide water. Too much stress can not be laid upon the fact that the people who must be depended upon to supply the demand for this grass for any future economic use, are already familiar with its habits of growth and the best methods of harvesting and curing it, and although the present employment of this material for house thatching is general throughout the Archipelago, yet the amount so used amounts to but a small fraction of the quantity which could be obtained under systematic methods of collection.

In my opinion it is absolutely out of the question to cut the grass by machinery in Tarlac Province and it is not advisable to bale it where it grows. If cut with sickles or short grass scythes and tied into bundles of about 20 pounds each, it is easily handled. One day in the sun is sufficient to cure the grass, then it may be loaded on carts and hauled to the railroad station. One native draft animal will haul 500 to 750 kilos (1,100 to 1,650 pounds) of rice and this weight of grass bundles is not too bulky for the carts now in use, if they are supplied with some kind of a bamboo rack. I have frequently seen ton lots of clean grass tied in many neat bundles 20 to 30 centimeters (8 to 12 inches) in diameter stored under roofs for future use.

The effect of decreased bulk upon freight rates up or down the road to the factory site would determine whether straw presses should be located at points on the railroad. I believe that it would be perfectly feasible to

collect this grass in car lots at several places along the main and branch lines of the Manila and Dagupan Railway; for instance at Capas and Tarlac the surrounding grass lands are tapped for from 5 to 10 miles each in two directions by fair roads at the season of the year when the grass is at its best, and before it is dry enough to be fired. One plan would be to erect bamboo framed storehouses with iron roofs near the freight tracks at these stations, for the storage of the grass as it is hauled in from the surrounding country.

Cogon grass is abundant and of good quality in the Visayan Islands. Thousands of acres of rolling lands are covered with even stands of tall, thrifty, cogon grass in Masbate and on the Island of Burias. Here the lay of the land is such that heavy draft mowing machinery could be used to advantage.

A practical phase of the utilization of Philippine perennial grasses would be in the material benefit to the forests, as the protection and cutting of the grass areas would greatly decrease the annual loss of forests by fire.

Cogon grass is not jointed like the cereal straws, which constitutes a great advantage in its use for paper pulp; its yield is 5 to 10 per cent higher than that of the latter, it is more easily pulped with the use of a less proportion of caustic soda. Another advantage is that in general, plants which are designed for fiber production should be harvested before the stems are fully mature; this is impossible when the plant is grown for production of grain, as is the case where straw, hemp, flax, etc., are utilized.

I have been asked what price could be offered for cogon grass as a paper material. This is very difficult even to approximate. It depends largely upon whether the grass were to be pulped and manufactured into paper for local consumption, or simply pulped for exportation, in which latter event it would have to enter in competition with chemical wood pulp. The average price paid for American pulp wood in 1905 was ₱11.10 per cord ($5.55 United States currency). A cord of pulp wood and 1,000 kilos (1 metric ton) of grass will produce approximately the same amount of unbleached pulp, namely 1,000 pounds; but the grass is easier handled, is fit for immediate immersion in the digesting vats, and it can be pulped by the same process of treatment, with one-half the expense in time and cost of chemicals. Furthermore, grass pulp will bleach to a good white with 6 to 12 per cent of bleaching powder, whereas wood pulp requires 12 to 25 per cent.

I would estimate that a paper pulp mill, if assured of a continuous supply of a sufficient quantity of clean grass, could pay approximately 1 peso (50 cents United States currency) per picul (137½ pounds) of clean, dry grass laid down at railway or waterway transportation. This is slightly in advance of the average price of American pulp wood.

INITIAL COST OF PULP AND PAPER MILLS.

Because of numerous inquiries from local sources on the probable initial cost of pulp and paper mills, it was thought best here to include some approximate estimates for the benefit of those interested. They are as accurate as the means at our command will permit them to be, but they must not be considered as being other than rough approximations.

*Preliminary estimate of a 10-ton sulphite wood pulp mill.*

| | |
|---|---|
| One digester, lined and fittings complete | $9,000.00 |
| Liquor making system, pumps, reclaimer, lead piping, gas coolers | 9,000.00 |
| One steam boiler for digester cooking | 2,700.00 |
| One centrifugal screen | 1,350.00 |
| One flat screen for tailings | 300.00 |
| Wood preparing machinery and knotter | 4,275.00 |
| Stock chests and stock pumps | 1,000.00 |
| Piping, steam fittings, shaftings | 3,500.00 |
| Fire and water pumps | 850.00 |
| Miscellaneous | 1,800.00 |
| | 33,775.00 |
| Plus 15 per cent for erection | 5,066.25 |
| | 38,841.25 |
| Power required, 200 horsepower, which if developed by steam will cost in addition to the above amount | 5,000.00 |

It must be borne in mind that a 10-ton plant requires nearly as costly machinery as one much larger, and in many other ways a 20-ton plant is to be considered more economical.

*Preliminary estimate of a ten-ton soda wood pulp mill.*

| | |
|---|---|
| One steel digester | $4,000.00 |
| Liquor making system, pumps, evaporators, causticizing tanks, calcining furnace, etc | 5,000.00 |
| All other items approximately the same as above estimate for sulphite mill | 15,775.00 |
| | 24,775.00 |
| Plus 15 per cent for erection | 3,716.25 |
| | 28,491.25 |
| Power required, 200 horsepower; if this is developed by steam, add | 5,000.00 |

This estimate would be reduced still further by substituting winnowing or glass-cleaning machinery for the expensive items of wood-preparing machinery, knotter, etc., for a mill manufacturing soda pulp from perennial grasses.

There should be added to the above pulp mill estimates for a complete plant for paper making:

| | |
|---|---|
| One Fourdrinier machine complete | $50,000.00 |
| Building, capital, etc | 50,000.00 |
| Miscellaneous paper making machinery, not included in pulp mill equipment, including refining engines, cutters, calenders, dryers, molds, presses, etc | 20,000.00 |
| | 120,000.00 |

The following is a summary:

| | |
|---|---|
| A 10-ton sulphite wood pulp and paper plant complete | $163,841.25 |
| A 10-ton soda wood pulp and paper plant complete | 153,491.25 |
| A 10-ton soda pulp and paper plant for manufacture of grass, straw and bamboo paper | 140,000.00 |

## GENERAL CONCLUSIONS.

Although the process of paper making is distinctly technical, yet it can not be said that the industry as a whole is operated on a strictly scientific basis. The establishments which employ trained chemists, men thoroughly grounded in the fundamental principles of the science and able to handle new problems, are comparatively few in number. A man capable of assaying bleach liquor or other chemicals used, is all that is required at the present time. However, I firmly believe that in a comparatively short time the lines of competition in this industry will be so closely drawn that the services of a chemical technologist will be necessary. The capacity of the average analyst employed in paper mills to handle technical problems is limited to work of a routine nature, although this is not always what is expected of him at times when unforseen difficulties arise. The most abstruse investigation may become the source of important practical progress.

We have prepared in this laboratory pulp boards and handlaid bleached and unbleached paper from the various raw materials, treated by both chemical processes, and samples are on hand for distribution to those who may be interested.

# ILLUSTRATIONS.

PLATE I.

[Photomicrographs by Martin. Fibers seen longitudinally.]

FIG. 1. Lauan (*Shorea contorta*).
2. Mayapis (*Anisoptera vidaliana*).
3. Cupang (*Parkia roxburgii*).
4. Dita (*Alstonia scholaris*).

FIG. 1.

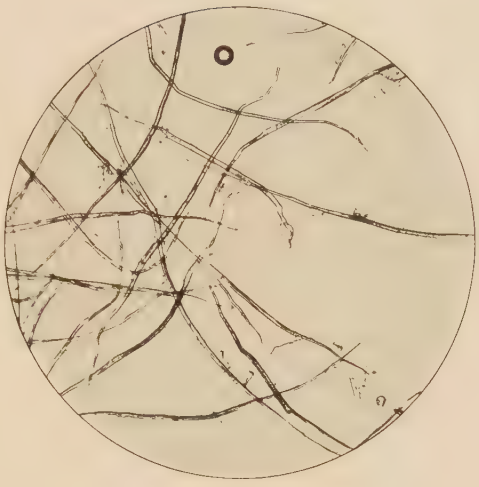

FIG. 2.

FIG. 3.

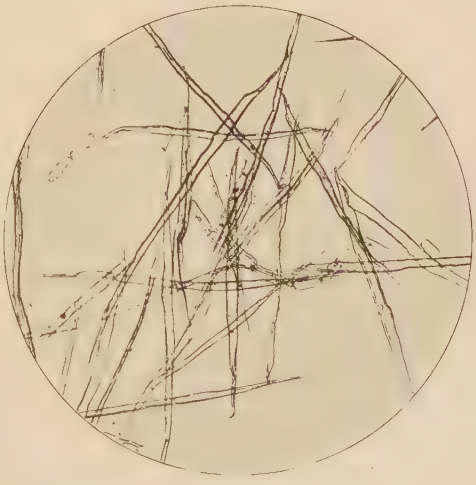

FIG. 4.

PLATE I.

# THE CRATER LAKES OF TAAL VOLCANO.

By Raymond Foss Bacon.

(*From the Chemical Laboratory, Bureau of Science, Manila, P. I.*)

About a year ago I published the results of analyses made on the nature of the interesting lakes in the crater of Taal volcano.[1] The water examined at that time was brought to the laboratory in January, 1906. Another expedition from this laboratory visited the volcano early in March, 1907, and it is the purpose of this paper to record the data then collected. During the intervening period no marked eruptions of the volcano had occurred, but it was nevertheless found that quite evident changes had taken place in the crater area; these are shown by a comparison of the photographs taken two years ago, one year ago and recently. (See Pls. II to VI.) The yellow lake, which existed in 1906 and of the water of which an analysis was given in the former communication, has entirely disappeared; even the lake bottom had been completely filled up so that there now is nothing to indicate that such a lake ever existed. Other places where small, red and green lakes were seen by the previous expedition, were also dry, although in most cases the lake beds were still sharply defined, the former bottom was covered with a thin, red or yellow crust which would not support a man, the stratum underneath being a soft, wet mud. The green lake has diminished in area, so that now access is possible to the two fumaroles at its south end; these are each about 10 meters in diameter at the surface, sloping conically to an opening into the earth of about 0.5 meter. From one of these blowholes a very large amount of steam not under great pressure is continually rising; from the other, much hot gas containing a large quantity of sulphur dioxide is issuing under considerable pressure and with a deafening, roaring noise. (See Pl. VI, fig. 3.) The two vents, which are not more than 15 meters apart, are evidently independent and not connected at any place near the surface.

To the southeast of the green lake, a basin is found in the present active crater, surrounded on three sides by high, perpendicular, rock walls, the least distance to the surface of the water being about 30 meters. The water of this lake is in constant, violent ebullition and

[1] *This Journal* I, 433.

great masses of steam and sulphur dioxide are continually rising from its surface, so that it is only possible to see it when a favorable wind blows the steam to one side; the water is covered with a greenish scum which is continually broken by the bubbles of steam and gas rising through it. The walls surrounding this crater lake are covered with an efflorescent deposit which is white, red, yellow, blue, and green in color and which is most probably not due to salts sublimed or distilled up on the rock walls from the boiling, acid lake below, it being formed by the action of the hot acid vapors on the lavas constituting the walls. That this is the case is shown by the fact that the colors of this deposit are stratified in a manner corresponding to the layers of lava. (See Pl. IV, fig. 2.) Sublimation would not in all probability have given such a stratification. This efflorescence consists of iron, aluminium and magnesium sulphates and chlorides and just as is the case with the water, aluminium is the predominant metal, iron coming next, and magnesium being present in moderate amount. In many specimens of this efflorescence the acid radicals have been lost, so that the residue is largely changed to hematites and clays. Oebbeke[2] in discussing the rocks from Taal speaks of the large number of feldspars and other aluminous rocks which he found in the neighborhood of the volcano, and gives the following analysis of the massive rock from Taal volcano:

*Analysis of massive rock from Taal volcano according to Oebbeke.*

| | |
|---|---|
| $SiO_2$ | 58.42 |
| $Al_2O_3$ | 17.64 |
| $Fe_2O_3$ | 5.66 |
| FeO | 4.00 |
| MnO | .48 |
| CaO | 4.50 |
| MgO | 2.54 |
| $Na_2O$ | 4.44 |
| $K_2O$ | 2.52 |
| $H_2O$ | .42 |
| $TiO_2$ | .31 |
| | 100.93 |

Mr. W. D. Smith of the Division of Mines of this Bureau tells me that he has examined rocks from Taal volcano and its immediate neighborhood, which contained large amounts of many classes of feldspars. These facts are mentioned as suggesting the source of the great quantity of aluminium salts and of alumina noted in the waters and in the effervescent deposits.

From a chemical point of view the striking aspect of the volcano consists in the large amount of salts of iron which are visible on all sides; the rocks being to a great extent colored to a red or yellow owing

[2] Beitr. z. Petrographie der Philippinen u. der Palau-Inseln, Stutt. (1881), 27.

to the deposition of components of iron salts showing such coloration; the deposits are to be found all over the volcanic island. We were unable to discover any sulphur in the crater of the volcano, although very perfect gypsum and alum crystals, colored to a sulphur yellow by salts of iron, were everywhere vigorously growing within the crater. Small fumaroles and fissures in the ground are situated all over the crater areas, even on the highest points on the walls; these emit steam and hot, sulphurous gases. The same class of efflorescent salt deposit as is encountered on the walls surrounding the boiling crater lake is encountered around the openings of many of these small vents. In examining these fumaroles it was noted that steam issued from some, whereas others gave off hot, sulphurous gases. No hydrogen sulphide was detected in the gases issuing from the various fumaroles in and around the crater, and the absence of any deposits of sulphur in the crater would suggest that this gas is never present, because, in the presence of the large amounts of sulphur dioxide, hydrogen sulphide, were it at any time a constituent of the volcanic gases, would certainly be decomposed to form sulphur.

Specimens of water were collected as follows: (*a*) From the boiling crater lake (Water No. 1); (*b*) from a green pool immediately to the north of this boiling lake (Water No. 2); and (*c*) from the green lake (Water No. 3).

*Water No. 1* is of a light grayish-green color; it is quite full of sediment, due to constant ebullition; its temperature is a little over 100° C.; it is very acid and possesses a strong odor of sulphur dioxide. It was much lighter in color than are the other waters, because sulphur dioxide is continually bubbling through the lake from which it comes, thus keeping the iron salts in almost a colorless, ferrous condition.

*Water No. 2* is of a deep green color. It was collected from one of a series of remarkable and formerly inaccessible pools which are found in what at first sight appears to be a filled-in extension of the boiling crater lake. What seems to be the northern beach of this lake consists of a crust of various colored iron and aluminium salts, in which numerous, small pools, 0.5 to 5 meters in diameter are encountered. These pools are of different colors—yellow, blue, green, and deep red. Some are boiling and are continually sending out small clouds of steam, while others in the immediate neighborhood are relatively cold. The one which was accessible, and from which the water which I analyzed was obtained, is boiling hot. The crust between these lakes will not support a man, hot water is present beneath it. It is remarkable that these pools should be so different in character, as is evidenced by their different colors and temperatures, when they occur in such close proximity to each other, with only apparently a thin, soft crust separating them. In fact, I was surprised to find the water of the pool which I examined to

differ from the waters of the crater lake proper, as the formation appears as if it were merely a part of the crater lake which had been filled in with colored salts through which the water still reached the surface in the remaining pools. This curious and beautiful formation is shown by Plate V, fig. 3, and Plate VI, fig. 2.

*Water No. 3,* from the green lake, is of a very deep, green color, it has a very strong, acid taste and, as obtained, it contained considerable sediment. However, farther from the shore the water is clearer. The sediment is largely clay and gypsum. All around the edges of this lake and covering the bottom near the shore, is a very abundant growth of gypsum crystals; the ones on the shores of the lake being colored yellow by iron salts.

Qualitative analyses demonstrated that all three waters contained the same elements, ferric and ferrous iron, aluminium, magnesium, calcium, strontium, barium (spectroscope), ammonium (small amount only), potassium, sodium, sulphuric and hydrochloric acids, and phosphoric acid (traces). No cæsium or rubidium or other rare or unusual elements could be detected by spectroscopic examination. The quantitative analyses are as follows:

TABLE No. 1.—*Quantitative analyses of water from the crater of Taal volcano.*

[Figures express grams per 100 cubic centimeters of the water.]

| | No. 1. | No. 2. | No. 3. |
|---|---|---|---|
| Color | Light grayish green. | Green. | Green. |
| Sp. gr. at 15° | 1.072 | 1.081 | 1.158 |
| Acidity | 1.33 N. | 1.335 N. | 1.78 N. |
| Acidity calc. as $H_2SO_4$ | 6.52% | 6.54% | 8.72% |
| Calc. as HCl | 4.84% | 4.87% | 6.49% |
| Total solids (filtered water) by heating to 110° for six hours | 8.576 | 10.1402 | 19.788 |
| | Per cent. | Per cent. | Per cent. |
| Chlorine, Cl | 4.7512 | 4.8925 | 10.9312 |
| Sulphuric ions, $SO''_4$ | 3.0808 | 1.9688 | 2.3542 |
| Ferrous iron, Fe | .5148 | .8367 | 1.1960 |
| Ferric iron, Fe | .0009 | .0843 | .1486 |
| Total iron | .5157 | .9210 | 1.3446 |
| Aluminium, Al | .7622 | .8978 | 2.0927 |
| Calcium, Ca | .2813 | .2082 | .1328 |
| Magnesium, Mg | .0318 | .4343 | .1514 |
| Sodium, Na | .7419 | .7192 | 2.3246 |
| Potassium, K | .0125 | .0048 | .0104 |
| Loss on evaporating to total solids | 2.1171 | .8284 | .8985 |

The "acidity" of these waters, as was that of the waters analyzed a year ago, was determined by titrating with $\frac{N}{10}$ alkali, using phenolphthaleïn as an indicator, and hence it does not represent the true acid value or even the extent of hydrolysis of salts taking place in these waters. This

will readily be seen if their composition is only casually considered. These lakes are largely solutions of aluminium and iron chlorides and sulphates. The determinations of the different elements were made directly, both in the present analyses and in the former ones, as it is evident that where iron and aluminium chlorides are present in such large quantities, analyses of the solid residues would not give the true composition of the waters; it is also evident that the total solids obtained by drying for six hours at 110° only approximately represent the quantities of salts originally present, for a solid residue obtained in this way can not give true values, because it is impossible to obtain constant weight unless the dish is heated for a sufficient length of time to drive off most of the combined chlorine, in which case iron and aluminium will also be lost.[3]

If one calculates the number of anion and kation forming elements from the analyses, some rather interesting and what at first appear to be rather surprising results, are obtained. In Water No. 1 the number of anions largely exceeds that of the kations and this would be expected, as sulphur dioxide is continually bubbling through the boiling crater lake. In Waters Nos. 2 and 3, as well as in the two which I examined last year, the number of kations exceeds the number of anions, but that this condition should exist and the waters still be very acid, seems to be contradictory. However, if the behavior of solutions of aluminium and iron chlorides on evaporation are considered, then the behavior of these waters at once becomes clear.

It is well-known that the so-called neutral salts of aluminium are very acid, acting on metallic iron or zinc just as do dilute acids; the salts of aluminium easily dissolve alumina to form basic salts [4] and from such salts, aluminium oxide and the various hydroxides are only gradually precipitated, the rate depending upon the concentration of acid present, the temperature and other factors.[5] The conclusion is therefore valid that basic salts of aluminium and iron are present in these waters, which are capable of sufficient hydrolysis to give hydrogen ions. It is hardly necessary to state that all determinations have been made in duplicate. The precipitation of alumina from such basic salts must take place with comparative slowness, for it was found that the salts in these waters were not yet in dynamic equilibrium. The filtered samples, analyzed

[3] It would be possible to determine the real amounts of free acid in these waters by a study of the electrical conductivity of these waters as well as of their constituent salts, obtaining the speed of migration of the various ions according to the methods developed by Bredig. Such a determination could also be made by a study of the hydrolysis of esters or of cane sugar.

Such a study would involve very many factors, and would consume so much time, that for the purpose of the present paper it was not considered advisable.

[4] Dammer: Handbuch der anorganischen Chemie (1893), 3, 91.

[5] Tomasi: *Bl. Soc. chim.* (Paris) (1882), (2) **37**, 443.

a little over a year ago, have stood in the laboratory in tightly closed bottles. The temperature of Manila varies only a few degrees during the year and in the laboratory one could safely state that the variation of temperature to which these bottled waters have been subjected has not been over 10° C. Nevertheless, a large amount of sediment, which was found to consist of aluminium hydrate and a little gypsum, had collected in each of the containers, and 3 liters of carefully filtered Water No. 3, left standing for one week in a tightly closed, glass-stoppered bottle, had deposited nearly 1 gram of sediment which also consisted of gypsum and aluminium hydrate.[6]

Very extensive deposits of a fine quality of kaolin are found in the immediate neighborhood of Taal volcano, near Los Baños and between Mount Maquiling and Taal Lake. It is suggested that these were probably deposited as a result of the disintegration of feldspars and other aluminous minerals by hot, volcanic waters, just as the Taal waters are now depositing compounds of aluminium.

The aluminium, magnesium, calcium, and iron in the Taal waters can readily be accounted for as a result of the action of acid waters on the feldspar rocks in the immediate neighborhood and the nature of the efflorescent deposits found on rocks around the crater lake and the various fumaroles makes such an assumption probable. It is at first difficult to imagine that the large quantity of chlorine could have had its source in anything but common salt, but the amount of sodium present in the waters is sufficient to combine only with approximately 0.2 to 0.33 of the chlorine, so that if the latter element really originated from sodium chloride, much of the sodium must have been taken up to displace other elements in the passage of the water through the rocks. Calcium seems the most probable element to have been so displaced, as gypsum crystals are growing very vigorously both in and around the lakes, and it is well known that an alkali metal, or a metal of the group of alkaline earths, can readily be displaced by another metal of one of these groups, the direction of the reaction depending upon the concentration of the elements in the surrounding waters and taking place according to the general laws of mass action.[7] Rümpler[8] was able to displace calcium by the alkali metals, on filtering sugar saps through various silicates, and he proved that the reaction was one which was readily reversible, its

[6] The extensive French deposits of bauxite are ascribed by Coquard and Angi to hot, mineral springs and geysers which dissolved the alumina and brought it to the surface. Hays ascribes the Georgia, Alabama, and the Arkansas deposits to the action of waters containing sulphuric acid, on aluminous shales and feldspars, the waters probably being neutralized by limestone after reaching the surface.

[7] Van Hise: A Treatise on Metamorphism. *Monograph U. S. Geol. Survey* (1904), 252.

[8] Rümpler: *Ztschr. Ver. Rübenzuck. Ind.* (1903), 798.

direction depending upon the concentration of the alkali metal and metal of the group of alkaline earths present in the solution. Nothing but the high chlorine content suggests the sea as a probable origin of the waters of the crater lakes of Taal. The volcano is quite near the sea, but the most eminent geologists incline to the view point that volcanic waters do not usually come from that source.[9]

It seems most improbable, therefore, to judge from the composition of the waters, that they originate in the sea, and it seems almost equally improbable that the chlorine is due to sodium chloride without making unproved assumptions, and consequently it is more rational to assume that these waters have come from the original magma of the volcanic core, for ferrous chloride occurs in meteorites, for example such as lawrencite,[10] a mineral which is easily decomposed.

## THE RELATIVE ABUNDANCE OF THE CHEMICAL ELEMENTS.

Clarke [11] says:

> The resemblance between meteoric stones and volcanic rocks is noteworthy. * * * The earth below its crust may be like a huge meteorite in composition, with the stony part predominating.

He calculates as the average percentage amount in the earth's crust of the principle elements mentioned here as follows:

| | |
|---|---|
| Chlorine | 0.01 |
| Magnesium | 2.68 |
| Iron | 5.46 |
| Sodium | 2.36 |
| Aluminium | 7.81 |
| Potassium | 2.40 |
| Sulphur | .03 |
| Calcium | 3.77 |

While the average amounts of chlorine and sulphur found in the earth's crust are very small, still it is well known that various elements are often concentrated in limited areas, as in the known cases of mineral deposits. Hence the fact that so small a percentage of chlorine and sulphur are found in the earth's crust as a whole does not invalidate the conclusion that these elements may have originated in the volcanic magmas at this point.

Van Hise makes the following statement:

> If at the time the earth stuff segregated, chlorine was contributed as laurencite, it is certain that the action of waters in the magmas upon this compound would produce hydrochloric acid; this suggests a source of a part of the hydrochloric acid of volcanos.

[9] Chamberlin and Salisbury: Geology (1904) **1**, 572.
[10] Van Hise: Metamorphism, 978.
[11] Bull U. S. Geo. Sur. **78**, 39.

He further says, concerning the origin of the various elements and compounds found in volcanos:

> The belt of weathering may be permeated locally with hot, gaseous solutions. The work of these gaseous solutions is of essentially the same nature as ordinary gaseous solutions, * * * but the gaseous solutions adjacent to igneous rocks usually contain a greater quantity of the active chemical agents than do ordinary solutions, and moreover their temperature is much higher than normal. This gives a combination which results in much more rapid alteration than the average of the belt of weathering, and alteration of a different kind * * *. It is to be presumed that the ultimate source of the various products found in the belt of weathering is the material of the original magmas. * * * Chlorine, hydrochloric acid, hydrofluoric acid and hydrosulphuric acid are undoubtedly largely formed by the action of hot water upon chlorides, fluorides and sulphides. Sulphurous and sulphuric oxides are produced by the action of the oxygen upon the sulphides.

Van Hise inclines to the view that the volcanic waters as well as the substances dissolved in them usually have their origin in the original magmas and he calls particular attention[12] to the kaolinization of feldspars by wet steam. This possible origin of the kaolin beds must be considered when we wish to arrive at conclusions regarding the origin of the extensive clay beds found in this active volcanic region. These speculations in regard to the origin of the substances found in the crater waters of Taal volcano are of interest, but naturally they can not be conclusive until much more extended investigations, which the Division of Mines of this Bureau plans soon to take up, have been completed. The very exceptional composition of these waters is made more evident by a search through the published reports of water analyses, for I have been unable to find any waters which even approach to them in composition. Many mine waters are markedly acid, but this is usually due to ferrous or other sulphates, which are ultimately referable to the decomposition of sulphides. I have been unable to find reported analyses of waters containing large amounts of aluminium, iron, and chlorine.

### A STUDY OF THE RADIO-ACTIVITY OF THE WATERS OF TAAL VOLCANO.

In my first paper on the Taal waters from the crater of Taal volcano, I gave the results of experiments which were all negative, to determine whether these waters are radio-active, but as these determinations were made about one month after the waters were collected they could not be considered as being conclusive. I was especially anxious to test these waters for radio-activity because of the recent theories which have been developed by Rutherford, Strutt and others in regard to the influence which the small amount of radium found in the earth's crust would have on the maintenance of the heat supply, and consequently I considered it of importance to study a hot, active volcanic area in regard to its

[12] Loc. cit. 493.

radium content. Since the first paper was published, Major Dutton [13] has advocated a theory that there is a causal connection between radio-activity and volcanos. A volcano is located in a part of the earth where, for some reason, radium compounds are concentrated, and he believes that the radium salts are the ultimate source of the volcano's heat supply. His arguments in favor of this theory are briefly as follows:

1. The solidity of the earth does not exactly correspond with other theories.

2. The comparative smallness of the extravasated masses in any single eruption is in favor of his view.

3. The repetitive nature of volcanic eruptions favors his contention. Why does not a volcano discharge all the material in one stupendous belch, and then close forever?

4. There is a growing mass of strong and highly concordant evidence showing that the seat of the reservoir is very shallow, it seldom being more than three miles in depth; the indications being that most of the volcanic eruptions originate at depths of between one to two and one-half miles. The evidence of this fact is furnished by the earthquakes which almost always accompany such eruptions.

We may now proceed to state the probable cause of volcanic eruptions. They are caused I conceive by a development of heat, resulting from radio-activity in limited tracts at a depth of 1 to 3—at the very utmost not over 4—miles from the surface, which is sometimes sufficient to melt the rocks affected by it. The melting is gradual, and when a sufficient quantity is melted, the water which it contains becomes explosive and usually suffices to break through the covering, constituting an eruption. When all the lava is erupted and the reservoir is exhausted it closes up for a time. If the heat continues to be generated, more lava is melted, and in due time another eruption occurs. The process may be repeated again. It may be repeated hundreds or thousands of times. The volcanic action may continue in the same place for hundreds of thousands or even millions, of years, or it may repeat itself only a few times, or may even occur only once.

Rausch von Trauenburg [14] made some observations on the crater of Vesuvius—the gases from which produced marked ionization and a prompt discharge of the leaves of the electroscope.

Loudebeck [15] has answered Major Dutton in so far as the geologic phases of the question are concerned. He shows that the composition of lavas is such as to preclude their having their origin at such slight depths in the earth, for they differ in chemical composition from the major sedimentary rocks, and hence must have originated below the zone of sedimentation.

If a volcano is such a center of radio-activity, a place where radium is so concentrated in the earth's crust that the rocks are melted by the perpetual heat store, then materials collected from a volcanic crater should be exceedingly active. Taal, which is an active crater, offers a good opportunity to test the theory. I have examined the waters collected by this expedition as well as the lavas, efflorescence and sediments. The apparatus used was like that described in the former paper, being an electroscope in a large chamber of the general type of instrument used

[13] *Journ. of Geol.* (1906), **14**, 259.

[14] Quoted by Dutton, *loc. cit.* Castovina (*Boll. Accad. Gioenia di Sc. nat. Catania* (1906) **84**, found rocks from Aetna slightly radio-active, the lavas the least so, the soil from the mountain slopes much more active.

[15] *Journ. of Geol.* (1906), **14**, 747.

by Elster and Geitel [16] and by Mache [17] and other European workers in their investigations on the radio-activity of ordinary materials. The normal rate of movement (air leak) of the gold leaf of the electroscope was forty divisions per hour and it was fairly constant over the period of the investigation. The waters were examined according to the methods of Mache,[18] air being sucked through the water, the emanation being drawn with it into the jar containing the electroscope. Waters Nos. 1 and 2 showed no trace of activity. Water No. 3 was slightly active, the gold leaf movement being increased by it to sixty divisions per hour. Barium sulphate precipitates, formed in these waters, were all inactive. In examining solids, 100 grams were generally placed in the jar containing the electroscope, according to the method used by Elster and Geitel [19] in testing clays and other materials. The sediments of waters Nos. 1 and 2 were inactive, that of No. 3 was active, the rate of movement of the gold leaf being increased to two hundred divisions per hour; it was five times the normal. The emanation obtained by decomposing the sediment with hydrofluoric and nitric acids, and then blowing air through this active specimen, fell to half the original value in about four days; this phenomenon corresponds to that exhibited by radium; the excited activity also fell to half value in about thirty minutes, which likewise points to radium as its source. For comparison one gram of uranium oxide (black, Kahlbaum) was placed in the apparatus, the rate of fall of the gold leaf was then one hundred per minute, or six thousand per hour. One gram of pitchblende from Joachimthal, containing 26.1 per cent of uranium, gave a rate of twelve thousand five hundred per hour, a magnitude which is about six times the rate per unit for uranium from the natural mineral, as compared with that from the chemical oxide. This rate agrees very well with that found by McCoy [20] as the ratio between a natural (uranium containing mineral) and a pure uranium salt.

Boltwood's determination of the amount of radium per gram of uranium in any natural mineral is $8\times10^{-7}$ grams. The sediment which I found to be active could then contain only $4.3\times10^{-11}$ gram of radium, a quantity which corresponds to $4.3\times10^{-13}$ gram of radium per gram of sediment.

Strutt [21] made tests on various igneous rocks from different parts of the world and found them all to show radio-activity, the most active being the more acid granites and syenites, the least active, basalts and various ultra basic rocks. The range in content is calculated at from $1.84\times10^{-12}$ to $25.5\times10^{-12}$ gram of radium per cubic centimeter of rock, or $0.613\times10^{-12}$ to $9.5\times10^{-12}$ gram of radium per gram of rock. Rutherford calculated that samples of soil examined by Elster and Geitel in Berlin contained $10^{-13}$ gram of radium per gram of soil.

[16] *Physikal, Zt. schr.* (1904) **5**, 321.
[17] *Monatsh. f. chem.* (1905) **26**, 595.
[18] *loc. cit.*
[19] *Loc. cit.*
[20] *Ber. d. chem. Ges.* (1904) **37**, 2641.
[21] *Proc. Roy. Soc. Lond. Sec. A.* (1906) **77**, 472.

It will be seen from the above that the sediment from water No. 3 is only very feebly radio-active, for it increases the natural air leak to only five times the normal rate. It is not at all uncommon to encounter clays and solids which increase it from fifty to one hundred times, in fact Elster and Geitel [22] found a comparatively immense amount of radium in the so-called "fango," a fine mud from hot springs in Battaglia, northern Italy. Natural carbonic acid obtained at great depths from old, volcanic soil was found to be radio-active by these observers. The famous medicinal hot springs of Europe have all been examined, and most of them have been found to be radio-active, but Curie and Laborde and others have examined hot springs which are not radio-active, so that the phenomenon is not entirely a general one.

I do not attach too great importance to the actual numerical value of the radium content of the sediment as it is calculated above, as the apparatus used was somewhat crude, but the numbers given agree pretty well with those obtained by others using a similar type of apparatus, but certainly the amount of radium in this sediment is extremely small. In fact Strutt, in examining various rocks, often found granites which gave a higher value than the one found by me. Therefore, as so little radio-activity was found in this one specimen, and especially as no trace of such activity existed in the boiling, crater lake, it must be concluded that Taal is a volcano which is not located over an area of a concentrated supply of radium, and that therefore Dutton's theory will certainly not apply to this volcano.

Another fact which argues very strongly against Dutton's view is the following: Radium is always associated with uranium or thorium. If there were enough radium present in a limited area to melt the rocks, this would also necessitate the presence of large amounts of uranium or thorium. Volcanic lavas and ejecta have repeatedly been examined by chemists, the analyses probably including thousands of specimens, and yet no great quantity of uranium or thorium has been encountered in them. If we calculate from the known radium content of pitchblende it becomes evident that if the heat given off by the minute amount of radium which is present were to accumulate to a sufficient extent to melt the rock, the latter would certainly need to be insulated in a much better manner than we have ever been able to obtain in practice, or indeed better than we have any reason to believe is possible within the earth's crust. Furthermore, there is no evidence that would lead us to believe that the radium content of any area could ever rise above that associated with a pure uranium mineral, that is a quantity which for each gram of uranium would represent $8 \times 10^{-7}$ gram of radium. The amount of radium occuring in a mineral, per ton of uranium, is 0.72 gram, and it has never been found to be more than this, it being probable that an

[22] *Physikal Ztschr.* (1903) **5**, 11.

equilibrium exists between uranium and radium with possibly actinium as an intermediate product. This much radium would evolve about 70 gram calories per hour,[23] an amount of heat which with perfect insulation, would require five hundred and forty days to increase the temperature of one ton of substance of specific heat 1, by 1°, but perfect insulation is not conceivable within the earth's crust.

The above calculation is based on the limit value of the heat which would be possible if we were to encounter a volcano of pure uranium, and which would therefore contain the maximum amount of radium which experimental facts at present show to be possible, and the amount of radium actually found in rocks and minerals is but $10^{-4}$ to $10^{-5}$ times this quantity.

In addition to these considerations the fact remains that the waters and sediments from the crater of Taal volcano were found to contain almost no radium.

[23] Rutherford: Radioactivity (1905), 419.

# ILLUSTRATIONS.

Plates I, II, and Plate III, fig. 2, and Plate IV, fig. 1, from photographs by Worcester.

Plate III, fig. 1, and Plate IV, fig. 2, from photographs by Freer.

Plates V and VI from photographs by Bacon.

PLATE I.

FIG. 1. View from the eastern shore of Lake Bombom across to Taal Mountain.

2. View of Taal volcano from Lake Bombom, which completely surrounds the mountain.

PLATE II.

FIG. 1. Eruption of Taal volcano of July 5, 1904. Note the position of the boiling lake to the right of the erupting crater.

2. Another phase of the eruption of July 5, 1904. This eruption was characterized by the large amount of mud ejected causing, at its height, a violent mud shower.

PLATE III.

FIG. 1. The same crater in September 1904. The eruption has almost completely died down. The boiling crater lake is shown on the right of the active cone.

2. The same crater on December 31, 1905. Almost all signs of activity have now disappeared and the crater is filled with water.

PLATE IV.

FIG. 1. Panoramic view of the whole crater of Taal volcano on December 31, 1905.

2. View across the boiling crater lake showing the stratified walls surrounding it, and the salt deposits on these walls, December 31, 1905.

PLATE V.

FIG. 1. Panoramic view of the whole crater of Taal Volcano on March 4, 1907. The crater active in the eruption of July 4, 1904, and full of water on December 31, 1905, is now seen to be dry and totally inactive. The boiling crater lake is increased in area, while the green lake has decreased in size. A new disturbance area seems to be breaking out to the left of the boiling crater lake.

2. View looking toward the boiling crater lake. In the foreground are seen some of the small pools referred to as the north beach of this lake.

3. The peculiar formation of colored, boiling pools separated by a crust of iron salts, called the north beach of the boiling crater lake.

PLATE VI.

FIG. 1. View looking down from the north upon the yellow lake, the two fumaroles and the boiling crater lake.

2. Looking down from the north upon the boiling crater lake. In the foreground is seen the peculiar formation of the north beach of this lake.

3. The two fumaroles at the head of the green lake. The yellow lake discussed in the former paper was situated to the left of these fumaroles. It is seen that no trace of it remains.

FIG. 1

FIG. 2

PLATE I.

FIG 1.

FIG 2.

PLATE II.

FIG. 1.

FIG. 2.

PLATE III.

FIG. 1

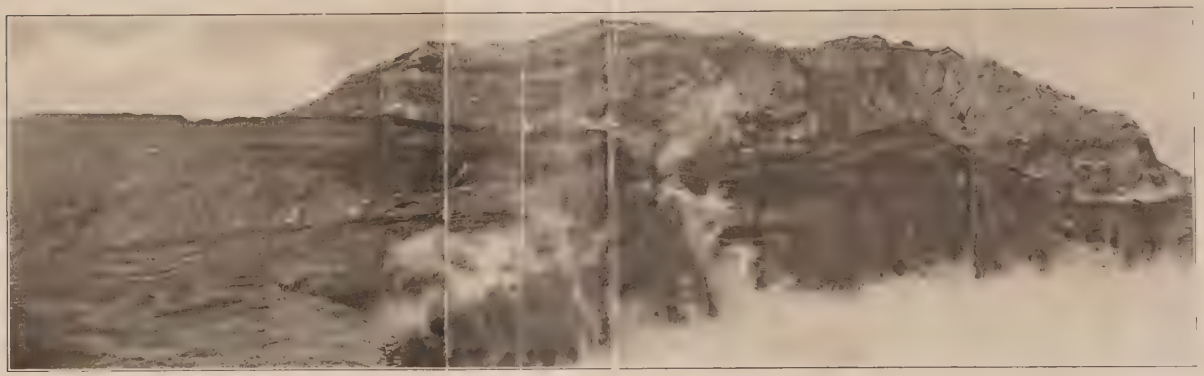

FIG. 2

PLATE IV.

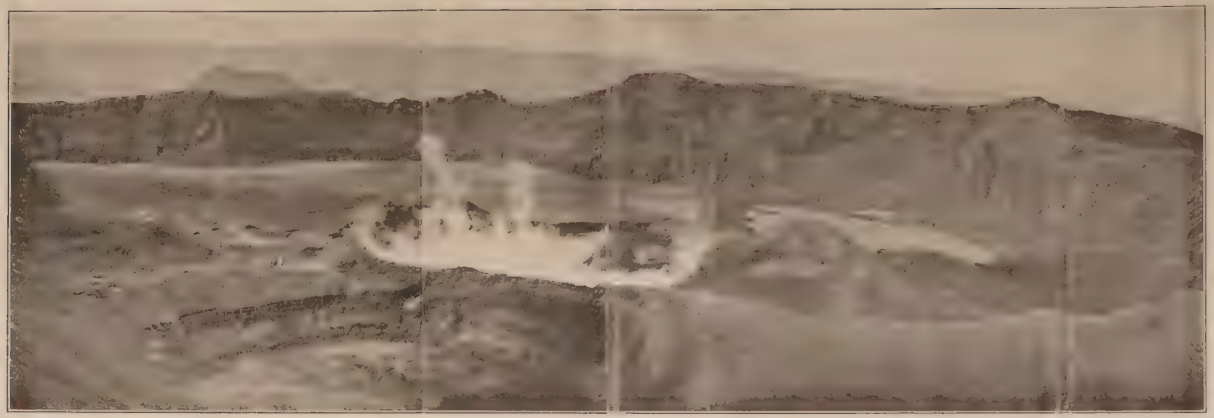

FIG. 1

FIG. 2

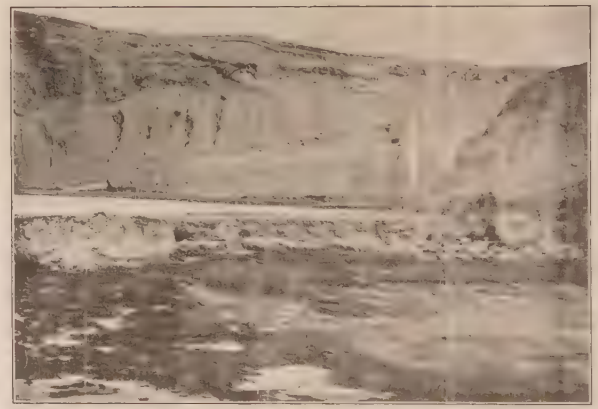

FIG. 3

PLATE V.

FIG. 1.

FIG. 2.

FIG. 3.

PLATE VI.

# CATALYSIS BY MEANS OF URANIUM SALTS IN THE SUNLIGHT.

By Raymond Foss Bacon.
(*From the Chemical Laboratory, Bureau of Science, Manila, P. I.*)

A few experiments were undertaken on the catalyzing effects of uranium salts in sunlight in conjunction with the study of the radio-activity of the waters from Taal volcano, described in the preceding paper. Seekamp [1] a great many years ago demonstrated that uranium salts acted as catalyzers in decomposing oxalic acid in the sunlight, but the same effect was not produced in the dark, even at 100°. The products of the catalysis were carbon monoxide, carbon dioxide, water and formic acid; on substituting succinic acid, Seekamp obtained propionic acid and carbon dioxide. Since the discovery of radium and of its capability of powerfully catalyzing many chemical actions, it becomes interesting to ascertain whether the catalytic action of uranium salts in the sunlight may not be due to the fact that uranium is one of the elements which forms radium and whether its power of catalyzing may not in some manner be connected with its radio-activity. As the sunlight of the Tropics afforded an exceptionally favorable opportunity, the following experiments were undertaken with the view of proving or disproving this supposition.

The apparatus consisted of a 100 cubic centimeter, graduated Ehrlenmeyer flask and a eudiometer. The flask was tightly closed with a well-fitting rubber stopper, through which a glass tube passed to the eudiometer. The gas was collected over the water. Two or more such flasks were usually placed in the sunlight simultaneously, and the time necessary to collect a certain number of cubic centimeters of gas was noted.

The fundamental experiment was instituted to give a comparison of the rate at which a certain quantity of uranium salt would act as a catalyser of oxalic acid, when it was compared with pitchblende containing the same amount of uranium, pitchblende being over five times as radio-active—measured by the electrical method—as the uranium salt. It would follow from this that, if radio-activity had any connection with the catalytic process, the rate of gas formation with pitchblende would be very much more rapid than it would be with uranium salt.

A few experiments were first made in the apparatus with oxalic acid alone, 5 grams being used in each instance, and it was found that sunlight

[1] *Am. Chem.* (*Liebig*), (1862) **122**, 113; (1865) **133**, 253.

decomposes pure oxalic acid so slowly, as compared with the speed of the reaction with uranium salts, that the autodecomposition may be altogether neglected in the present series of experiments.

This result is in accord with those obtained by Richardson[2] who found that oxalic acid is only slowly decomposed by sunlight even at 0°, to form carbon monoxide, carbon dioxide, and hydrogen peroxide. The reaction does not take place under the red rays of the spectrum alone; sterilization has no effect, so that microorganisms take no part in it, although it is known that certain microörganisms decompose oxalic acid under proper conditions, to give carbon monoxide, carbon dioxide and water. No hydrogen peroxide is formed in the dark, even if oxygen is present. Dilute sulphuric acid does not decompose oxalic acid in the absence of light, as was proved by drawing air for seven days through a solution of the acid and into one of barium hydroxide, the oxalic acid being kept at 70° to 80°. Dilute sulphuric acid accelerates the decomposition of oxalic acid in the sunlight, for, in seven days, 0.06 gram of carbon dioxide was obtained from 5 grams of oxalic acid.

The reactions catalyzed by uranium salts are in the great majority of cases well known, taking place with extreme slowness when no catalyzer is present.

*Experiment 1.*—August 22. Direct sun from 2 to 2.45 p. m. To determine the effect of varying quantities of uranium salts on the speed of the reaction. Quantities in cubic centimeters.

(*a*) 5 grams oxalic acid.
2.2245 grams crystallized uranium acetate (Kahlbaum).
100 cubic centimeters water.
(*b*) 5 grams oxalic acid.
1.1386 grams uranium acetate.
100 cubic centimeters water.

| (*a*) | (*b*) |
|---|---|
| 45 | 40 |

When placed in diffused light in the laboratory (*a*) gave no more gas (*b*) gave 2 cubic centimeters.

*Experiment 2.*—August 30. Both flasks (*a*) and (*b*) were left in partial sunlight for fifteen minutes. One cubic centimeter of gas had collected in each one. On placing the flasks in the diffused light of the laboratory, gas continued to be formed for two hours, the amount being 12 cubic centimeters and 7 cubic centimeters, respectively, for (*a*) and (*b*). After placing a solution in the sunlight it takes some time for the reaction to attain its maximum rate, a fact which has often been noted concerning it. An oxalic acid solution containing uranium salts gives no gas, even at 100°, if it is kept in the dark.

*Experiment 3.* The solutions (*a*) and (*b*) were the same; the number of cubic centimeters of gas obtained from the two solutions in the same length of time and under the same conditions of sunlight were:

| (*a*) | (*b*) |
|---|---|
| 33 | 28 |
| 10 | 11 |
| 17 | 12 |
| 13 | 10.5 |
| 33 | 28 |

[2] *J. Chem. Soc.* (1894) **65**, 451.

It is therefore evident that the relative amounts of uranium salt only slightly affect the speed of the reaction.

*Experiment 4.*—Two cubic centimeters of concentrated nitric acid added to (*b*). Quantities in cubic centimeters.

| (*a*) | (*b*) |
|---|---|
| 32 | 27 |
| 16 | 11.5 |

*Experiment 5.*—Two quantities of solution (*a*) were compared with a solution containing 5 grams of oxalic acid and 2 grams of pitchblende, dissolved in the smallest possible quantity of nitric acid. The solution containing pitchblende (*b*) decomposed the oxalic acid at one half the rate of (*a*).

*Experiment 6.*—

(*a*) 5 grams oxalic acid.
100 cubic centimeters water.

(*b*) 5 grams oxalic acid.
2 grams thorium nitrate.
100 cubic centimeters water.

In one hour and thirty minutes in sunlight, each gave 0.5 cubic centimeter gas. The thorium nitrate was but slightly dissolved and the solution was very milky in appearance.

*Experiment 7.*—To each of solutions (*a*) and (*b*) from experiment 6, 5 cubic centimeters of concentrated nitric acid was added partially to dissolve the salt of thorium, the time in sunlight being two hours. Quantities in cubic centimeters.

| (*a*) | (*b*) |
|---|---|
| 1.2 | 14 |

As the thorium salt is only slightly dissolved, this fact may have rendered the reaction in (*b*) slower than it otherwise would be, but nevertheless it is interesting to note that the radio-active thorium salts catalyze a solution of oxalic acid.

*Experiment 8.*—It was thought that possibly the increased rate of reaction observed in (*b*), experiment 7, might be ascribed to the action of finely divided particles of thorium nitrate as catalyzers. Hence, two flasks were prepared each containing 5 grams of oxalic acid dissolved in 100 cubic centimeters of water. To one of these freshly precipitated barium sulphate was added; to the other, finely ground silica, but no gas was obtained in either flask, even in the sunlight.

*Experiment 9.*—October 22, p. m.

(*a*) 4.31 grams pitchblende from Joachimsthal, containing 1.126 grams uranium dissolved in 5 cubic centimeters of concentrated nitric acid.
5 grams oxalic acid.
100 cubic centimeters water.

(*b*) 2 grams uranium acetate containing 1.126 grams uranium.
5 cubic centimeters concentrated nitric acid.
5 grams oxalic acid.
100 cubic centimeters water.

Quantities in cubic centimeters.

| Time. | (*a*) | (*b*) |
|---|---|---|
| 3.25 to 3.40 | 5.5 | 0.5 |
| 3.40 to 3.55 | 19.0 | 1.0 |

October 23, a. m. The tubes were now placed in the laboratory in diffused light; the next morning at 7.50 the reading was—

| (*a*) | (*b*) |
|---|---|
| 35.0 | 6.0 |

At 8 a. m. they were again placed in the sunlight.

| Time. | (*a*) | (*b*) |
|---|---|---|
| 8.00 to 8.20 | 18 | 3 |
| 8.20 to 8.30 | 35 | 12 |
| 8.30 to 8.38 | 12 | 17 |
| 8.38 to 8.45 | 25 | 40 |
| 8.48 to 8.56 | 10 | 31 |
| 8.59 to 9.14 | 25 | 40 |
| 9.16 to 9.30 | 26 | 36 |
| 9.32 to 9.44 | 22 | 38 |
| 9.46 to 9.56 | 22 | 38 |
| 9.59 to 10.12 | 22 | 37 |
| 10.14 to 10.25 | 22 | 36 |
| 10.27 to 10.43 | 22 | 36 |
| 10.45 to 10.59 | 25 | 38 |
| 11.01 to 11.12 | 24 | 38 |
| 11.42 to 11.58 | 25 | 40 |

October 23, p. m. The tubes stood in the diffused light of the laboratory from 12.00 to 1.00.

| (*a*) | (*b*) |
|---|---|
| 8.5 | 24.5 |

Therefore (*a*) in two hundred and forty-five minutes gave 297 cubic centimeters of gas, as compared with 561 cubic centimeters obtained from (*b*). The solution containing the pitchblende had the greater initial velocity which may possibly be due to the presence of iron salts, because the latter at first markedly catalyze solutions of oxalic acid, as is shown by later experiments given below, but radioactivity would seem to have little or no influence on the rate of the reaction, a conclusion which is confirmed by other experiments of the same character; the solution derived from pitchblende always exhibiting a slower rate than the ones containing uranium salts.

*Experiment 10.*—October 24, p. m.

(*a*) 1 gram ferric chloride (sublimed).
5 grams oxalic acid.
100 cubic centimeters water.

(*b*) 5 grams oxalic acid.
100 cubic centimeters water.
Picric acid added sufficient to give a color as nearly as possible like that of the uranium acetate solution used in (*b*), experiment 9.

| Time. | (*a*) | (*b*) |
|---|---|---|
| 1.25 to 2.15 | 40 | 0.5 |
| 2.26 to 3.20 | 40 | 0.5 |

The next morning the two tubes were place in sunlight at 8.00 a. m.

| | (*a*) | (*b*) |
|---|---|---|
| At noon | 2 | 0.7 |

This result is characteristic of iron salts when they are used as catalyzers in decomposing solutions of oxalic acid; at first the reaction proceeds quite rapidly, but it becomes slower until finally it is almost imperceptible.

Solution (*b*) was colored as given above because it was thought that perhaps the color of the uranium solution might have some connection with the absorption of the energy of the sunlight and consequently with the catalysis. This idea was especially suggested because ferric chloride, which also acts as a catalyzer in this reaction, is likewise yellow. Another solution, colored yellow with aniline yellow (Grübler & Co.) likewise gave negative results.

It was thought that possibly the ionization of the oxalic acid or of the water might be increased in the sunlight, and that this change in conditions might have an effect on the reaction. Nichols and Merritt [3] have recently demonstrated that fluorescent solutions conduct the current better in the sunlight than in the dark. Fluorescent substances absorb light and do not follow Kirchoff's law; nonfluorescent substances do not increase the conductivity in sunlight. The amount of fluorescence and conductivity are proportional to one another. Unfortunately, the original paper is not accessible to me, so that I was not able to follow the experimental methods employed by the authors, but I measured conductivities of boiling uranium solutions in the sunlight and in the dark in the usual Kohlrausch cell. No difference could be detected between the sunlight and darkness. I also studied the speed of hydrolysis of ethyl acetate by water at a boiling temperature in the sunlight and in darkness. No increase in the ionization of water in the sunlight could be detected by this method, nor does sunlight have any effect on the speed of esterification of ethyl acetate from glacial acetic acid and alcohol.

*Experiment 10.*—p. m.

(*a*) 1 gram ferric chloride sublimed.
5 grams oxalic acid.
100 cubic centimeters water.
(*b*) 2 grams ferric chloride sublimed.
5 grams oxalic acid.
100 cubic centimeters water.

| Time. | (*a*) | (*b*) |
|---|---|---|
| 2.10 to 3.00 | 13 | 40 |
| 3.02 to 3.25 | 23 | 40 |
| 3.30 to 3.53 | 20 | 33 |

[3] *Phys. Rev.* (1905) **19**, 396.

No gas collected when the solutions were left standing over night. Both were heated to 100° in the morning and then placed in the sunlight.

| Time. | (*a*) | (*b*) |
|---|---|---|
| 8.30 to 10.00 | 0.5 | 2.0 |
| 10.00 to 11.00 | .5 | 5.0 |

The marked falling off in the catalysis with ferric salts may be connected with the formation of a precipitate of ferrous oxalate which soon appears in the solution.

It would seem probable that the decomposition of oxalic acid takes the course of first evolving carbon dioxide and leaving formic acid and that the latter then breaks down into carbon monoxide and water, but formic acid with uranium acetate as a catalyzer gave no gas. As formic acid can be demonstrated to be present during the catalysis of oxalic acid by uranium salts, its formation is probably due to the reaction:

$$CO+H_2O=HCOOH$$

accelerated by uranium salts as a catalyzer.

The further study of this phase of the reaction is of considerable importance both from a theoretical and a practical standpoint.

Oxalic acid when treated with potassium bichromate, gives off gas even in the dark, but there is no decomposition either in the dark or sunlight with chromic chloride or with copper sulphate.

*Experiment 12.*—A study of the decomposition of potassium permanganate in the presence of uranium salts was next undertaken with a solution which contained approximately 4 grams of potassium permanganate per liter. (1 cc=0.00697 Fe.)

(*a*) 25 cubic centimeters potassium permanganate solution

(*b*) 25 cubic centimeters potassium permanganate solution and 10 cubic centimeters water.

(*c*) 25 cubic centimeters potassium permanganate solution, 0.1 gram uranium acetate and 10 cubic centimeters water.

The solutions were placed in the sunlight from 11.15 a. m. to 1.05 p. m., then 40 cubic centimeters of ferrous sulphate solution were added to each, by which means all were decolorized, and they were then titrated back with permanganate.

Number of cubic centimeters of permanganate required:

| (*a*) | (*b*) | (*c*) |
|---|---|---|
| 3.2 | 3.3 | 3.3 |

Uranium salts therefore have no effect on this reaction.

It is well known that reactions involving oxidation and reduction are usually very susceptible to catalyzers, and that many substances such as alkaloids, ammonium salts, sugars, etc., act as if they were poisons for the latter; whereas copper and iron salts usually accelerate the rate.[4]

[4] Young: *J. Am. Chem. Soc.* (1902), **24**, 301.

Some alkaloids also have a similar "poisoning" effect on the decomposition of oxalic acid in the presence of uranium salts in the sunlight.

*Experiment 13.*—

(*a*) 4 grams oxalic acid.
1 gram uranium acetate.
100 cubic centimeters water.

(*b*) Same as (*a*) but with 0.1 gram of brucin added. Measurements in cubic centimeters.

| Time. | (*a*) | (*b*) |
|---|---|---|
| a. m. 8.08 to 9.10 | 47 | 30 |
| 10.22 to 10.45 | 48 | 29 |
| 10.48 to 11.05 | 52 | 35 |
| 11.08 to 11.25 | 54 | 29 |
| 11.28 to 11.42 | 50 | 29 |
| 11.44 to 12.00 | 48 | 26 |
| p. m. 2.55 to 3.25 | 54 | 32 |
| 3.30 to 4.00 | 50 | 25 |

Brucin oxalate separates as white, crystalline needles when brucin is added to the solution, so that the concentration of the alkaloid was less than was represented by the amount added.

*Experiment 14.*—The same solution as in experiment 13, excepting that quinine was substituted for brucin in (*b*). Quantities in cubic centimeters.

| Time. | (*a*) | (*b*) |
|---|---|---|
| a. m. 8.15 to 9.20 | 71 | 27 |
| 9.24 to 9.50 | 76 | 21 |
| 9.53 to 10.20 | 77 | 20 |
| 10.23 to 10.45 | 68 | 18 |
| 10.48 to 11.10 | 75 | 20 |

*Experiment 15.*—In this experiment 1 gram atropin was substituted for brucin and a third solution (*c*) had added to it 0.2 gram cinchonin. Quantities in cubic centimeters.

| Time. | (*a*) | (*b*) | (*c*) |
|---|---|---|---|
| a. m. 11.25 to 12.00 | 81 | 20 | 13 |
| p. m. 2.20 to 3.50 | 108 | 40 | 14 |
| a. m. 10.40 to 11.20 | 84 | 34 | 12 |
| p. m. 1.00 to 1.40 | 78 | 34 | 12 |
| a. m. 8.00 to 8.45 | 72 | 30 | 10 |
| 8.50 to 9.30 | 81 | 40 | 12 |
| 9.40 to 10.15 | 82 | 33 | 8 |
| 11.25 to 12.00 | 80 | 33 | 7 |

*Experiment 16.*—(*a*) Standard solution. (*b*) With 0.1 gram morphine. (*c*) With 0.1 gram strychnine. Quantities in cubic centimeters.

| Time. | (*a*) | (*b*) | (*c*) |
|---|---|---|---|
| p. m. 1.15 to 1.37 | 51 | 32 | 32 |
| a. m. 8.30 to 9.30 | 102 | 27 | 34 |
| 9.33 to 10.10 | 103 | 38 | 40 |

I was surprised to discover, as is shown by experiment 1, that the quantity of uranium salt present did not markedly affect the rate of the decomposition of oxalic acid, but it was even more curious to find that the amount of oxalic acid also had relatively little effect.

*Experiment 17.*—

(*a*) 4 grams oxalic acid.
1.753 grams uranium acetate.
100 cubic centimeters water.
(*b*) 2.5 grams oxalic acid.
1.753 grams uranium acetate.
100 cubic centimeters water.

| Time. | | (*a*) | (*b*) |
|---|---|---|---|
| a. m. | 9.24 to 10.02 | 30 | 20 |
| | 10.04 to 10.20 | 31 | 27 |
| | 10.22 to 10.43 | 38 | 35 |
| | 10.45 to 11.08 | 31 | 30 |
| | 11.10 to 11.30 (shady) | 21 | 21 |
| p. m. | 1.35 to 2.01 | 35 | 29 |
| | 2.03 to 2.22 | 32 | 32 |
| | 2.25 to 2.46 | 32 | 30 |

Quantities in cubic centimeters.

*Experiment 18.*—

(*a*) 7 grams oxalic acid.
1.753 grams uranium acetate.
100 cubic centimeters water.
(*b*) 2.5 grams oxalic acid and the same amounts of uranium acetate and water as in (*a*).

| Time. | | (*a*) | (*b*) |
|---|---|---|---|
| a. m. | 9.00 to 9.45 | 35 | 25 |
| | 9.47 to 10.04 | 33 | 29 |
| | 10.07 to 10.28 | 34 | 30 |
| | 10.30 to 10.40 | 32 | 24 |
| | 10.43 to 11.08 | 32 | 24 |
| | 11.28 to 11.45 | 38 | 32 |
| p. m. | 1.32 to 2.00 | 33 | 12 |
| | 2.03 to 2.25 | 35 | 13 |
| | 2.27 to 2.50 | 35 | 11 |

There is therefore relatively little difference in the initial rate of the reaction, but as it proceeds, a marked variation begins to be noted.

I have also made few preliminary observations on the action of uranium acetate in the sunlight, on the decomposition of several organic acids. Propionic acid very slowly gives off carbon dioxide, mixed with a combustible gas which is probably ethane, but the amount which I had at my disposition was too small to identify. Wisbar [5] has shown that *n*-butyric acid gives propane and carbon dioxide. Tartaric acid evolves carbon dioxide quite rapidly and among the decomposition products

[5] *Ann. Chem.* (*Liebig*) (1891), **262**, 232.

acetaldehyde and pyruvic acid $CH_3.CO.COOH$ were detected, the presence of the latter being determined by obtaining the phenylhydrazone melting at 188°.

Pyrotartaric acid is also markedly decomposed, carbon dioxide being evolved, and *n*-butyric and isobutyric acids remaining; malic and lactic acids both give carbon dioxide and probably acetaldehyde, but the other products have not yet been determined. It is not unreasonable to suppose that the first decomposition product formed by the action of a uranium salt in the sunlight on malic acid, is lactic acid which is then further broken down to give acetaldehyde and formic acid.

Mandelic acid decomposes vigorously, benzaldehyde and benzoic acid being obtained in considerable quantity, the benzoic acid presumably resulting by oxidation of the benzaldehyde, for benzaldehyde is rapidly changed to benzoic acid by the tropical sun.

In each of two 250 cubic centimeter Ehrlenmeyer flasks 50 grams benzaldehyde was placed. One flask was put in the dark and the other in sunlight for one week; at the end of this time 2.2 grams and 18.5 grams of benzoic acid respectively had been formed.

It is noticeable that the tropical sunlight greatly accelerates the reaction. The same effect has been noted with a very high frequency electric discharge. Citric acid give off carbon dioxide, acetone being detected among the reaction products; trichlorlactic acid easily produces chloral hydrate; malonic acid gives acetic acid; all of the above with the evolution of carbon dioxide; phthalic and cinnamic acids are not acted upon, probably because of their insolubility.

These few experiments demonstrate the powerful catalytic action of uranium salts in sunlight; a solution of a uranium salt could probably be used as a chemical photometer. I consider the action probably to be intimately connected with the fluorescent nature of the solutions of these salts. The observations given above are very incomplete but as researches of greater economic value to the Philippine Islands are more pressing, I have abandoned the work for the present. It is evident that many reactions can be studied to far greater advantage in the Tropics than in the Temperate Zone, so that a new field for tropical investigation is opened.

# A NEW COMPARATOR.

By Alvin J. Cox.

*(From the Chemical Division, Bureau of Science, Manila, P. I.)*

Prof. Dr. Weinstein[1] says that in the construction of a comparator the following things must be taken into consideration: "(1) The external conditions, under which the comparison of the measures is made, (2) the construction of the measuring apparatus (microscope, micrometer), (3) the properties of the bars investigated." With regard to the first and last points, if the bars compared have the same coefficient of expansion, then it is only necessary to examine them at the same temperature. This is not difficult, for the external conditions can be controlled by the isolation of the cathetometer room and the exercise of due care.

There remains the construction of the apparatus to be considered. The demand for a great many provincial and other secondary standards in connection with the initiation of the new Weights and Measures Law of the Philippine Islands has made indispensable to this Bureau an instrument which could be depended upon to give comparisons with the standard meter bar, accurate within a few numbers in the second decimal of a millimeter. A high grade cathetometer similar to many[2] of those especially designed for making eudiometer readings was tried, but found unsatisfactory for our purposes. The one used is described by Gerhardt[3] as—

> A cathetometer with millimeter divisions of one meter length which at 0° is correct to 0.01 millimeter. The vernier permits a reading of 0.1 millimeter. The telescope turns in a plane exactly at right angles to the upright bar and the level upon the top has a sensibility of twenty seconds. For the first adjustment of the instrument there is a circular spirit level on the base. The telescope, etc., are perfectly balanced. The micrometer is so constructed that the possibility of an inclination of the telescope with the adjustment of the micrometer screw is excluded. Both the bar and the travel are perfectly straight, so that there is no turning of the telescope by moving up and down.

[1] Weinstein: *Deutsche Mechaniker Ztg.* (1899) (Berlin), 28.

[2] Terquem, A.: *Journ. de Phys.* (1883), **12**, 496. Miller, F.: *Ztschr. f. Instrumentenkunde* (1883), **3**, 409. Fues, R.: *Ibid.* (1886), **6**, 153. Wadsworth, F. L. O.: *Am. J. Sc.* (1896), **151**, 41.

[3] Gerhardt, C.: Preisverzeichnis über Chemische Apparate und Gerätschaften (1905), 13th Ed., 119, Bonn.

This instrument is shown in Plate I, fig. 1. It is not sufficiently accurate for the comparison of measures of length, because the adjustment of the level when the telescope is moved from one end of the upright bar to the other is necessary.[4] The range of the telescope is from three to five meters and with a level, the fineness of which is twenty seconds, makes possible an error of nearly a millimeter. This is the best level usually obtainable for this class of instrument, although sometimes one sensitive to fifteen seconds is used.[5] Even this would not be sufficiently accurate.

As a rule the superiority of an apparatus is proportional to its cost and in this case it was discovered that the only instruments made at present which could entirely satisfy our requirements were very expensive and much more complicated than needed. One was therefore constructed after the following plan and I think for a simple apparatus, it has features worthy of note.[6] In it the general method of comparison now employed in nearly all of the most accurate linear measurements is followed; that is, the length to be measured is placed parallel with the standard bar and the images of the linear lines of the two brought successively into the field of the observing microscope and their relative positions determined. In the forms of the cathetometers previously referred to, this has been done by observing the length to be measured in the telescope and at the same time the scale on the long vertical axis.

The new arrangement is shown in Plate I, fig. 2. In this apparatus the short leverage of the sliding parts and the angular displacement of the telescope are obviated. The base and upright travel columns for the crosshead are the base and standards of a Doolittle torsion viscosimeter.[7] The crosshead is supported by wires, passing over two wheels of the same size with a common axis mounted on a frictionless bearing, and exactly counterbalanced by leaded weights. The bars to be compared are suspended from the arch by vertical adjustible screws, in turn horizontally controlled by thumbscrews from the front and back. The lower ends of the bars are held in place by appropriate clamps. The microscope is mounted on a travel on the crosshead. With the horizontal motion of this travel and the vertical movement of the crosshead, freedom is obtained for the microscope over the entire plane bounded by the vertical columns of the apparatus. The microscope itself has a magnification

[4] This may have been partially due to the heat radiated from the operator expanding the side of the bar nearest him.

[5] *Ztschr. f. Instrumentenkunde* (1905), **25**, 16.

[6] Constructed in the workshop of the Bureau of Science, Manila, P. I., by Mr. J. A. Gilkerson, Chief Engineer, Bureau of Science.

[7] Doolittle, O. S.: *J. Am. Chem. Soc.* (1893), **15**, 173; *J. Soc. Chem. Ind.* (1893), **12**, 709. Wiley, H. W.: Principles and Practice of Agricultural Analysis (1897), III, 343, Easton, Pa.

of sixty diameters and a field of one and two-tenths millimeters. A glass plate graduated into millimeters is adjusted in the microscope tube so that a millimeter here is exactly equal to a tenth of a millimeter in the field, that is, these lines divide the field of the microscope into twelve equal divisions as shown in fig. 1. The glass plate serves as a micrometer

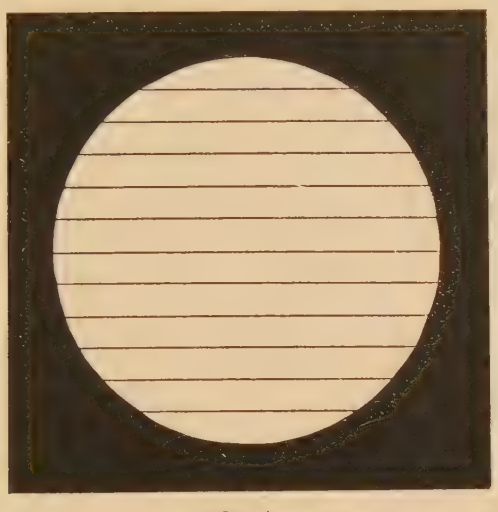

FIG. 1.

device; by its means tenths of a millimeter can directly be read and the variations between the two bars observed, as they are successively brought into the field. For the illumination of the bars a small electric light (not shown in the plate) is mounted just in front of their graduated surfaces during the reading. The zero points of the rods are adjusted by the screws at the top and are then quickly paralleled by passing the microscope downward along the edges of the bars and the lower ends brought into focus by adjusting the clamps.

This apparatus could be modified to operate satisfactorily in a horizontal position. The reason for making it vertical was to have vertical suspension and avoid the irregularities and inaccuracies produced by sagging or slight bending of the bars; also so that only the upper edge of the microscope travel need be perfectly fitted. At a greater expense an absolutely level table could be constructed for a horizontal apparatus, the microscope travel perfectly adjusted, the whole operated in a thermostat, and therefore the temperature perfectly controlled. With a horizontal apparatus, the adjustments of the bars could possibly be made more quickly.

It is thought that the plan of the double freedom of the microscope possesses many advantages over the stationary microscope and traveling track of other comparators, for example the comparator after Abbe.[8]

[8] *Ztschr. f. Instrumentenkunde* (1892), 12, 311.

With both the vertical and the horizontal apparatus the error of taking the observations is reduced to a minimum, both because of the close range of the microscope and the short displacement between the two bars to be compared. There is practically no liability of disturbing the adjustment while manipulating the microscope. A series of experimental comparisons were made and readings to a hundredth of a millimeter showed no error in the vertical instrument. This apparatus is thoroughly satisfactory for the testing of secondary standards. If it is desired to compare with the greatest accuracy that has yet been obtained, then it is recommended to follow the elaborate and more expensive plan of the Kaiserliche Normal-Aichungs-Kommission.[9]

[9] *Ztschr. f. Instrumentenkunde* (1895), **15**, 313 and 353.

# ILLUSTRATIONS.

PLATE I.

FIG. 1. A cathetometer of standard type.
2. A new comparator.

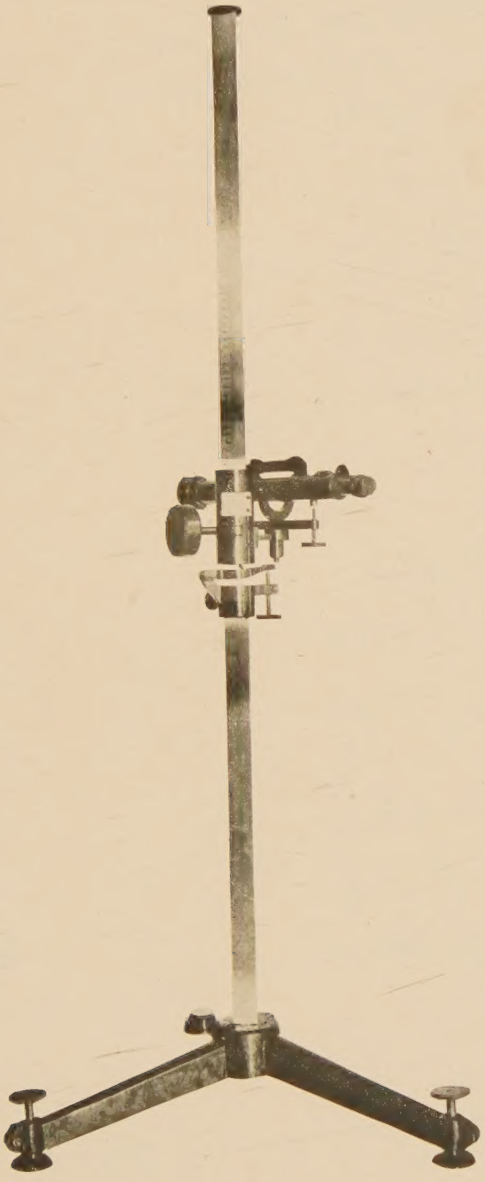

Fig. 1.

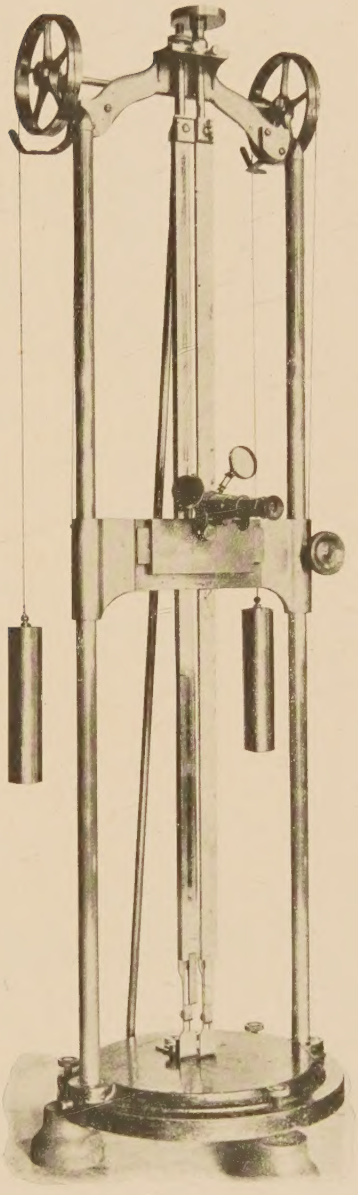

Fig. 2.

PLATE I.

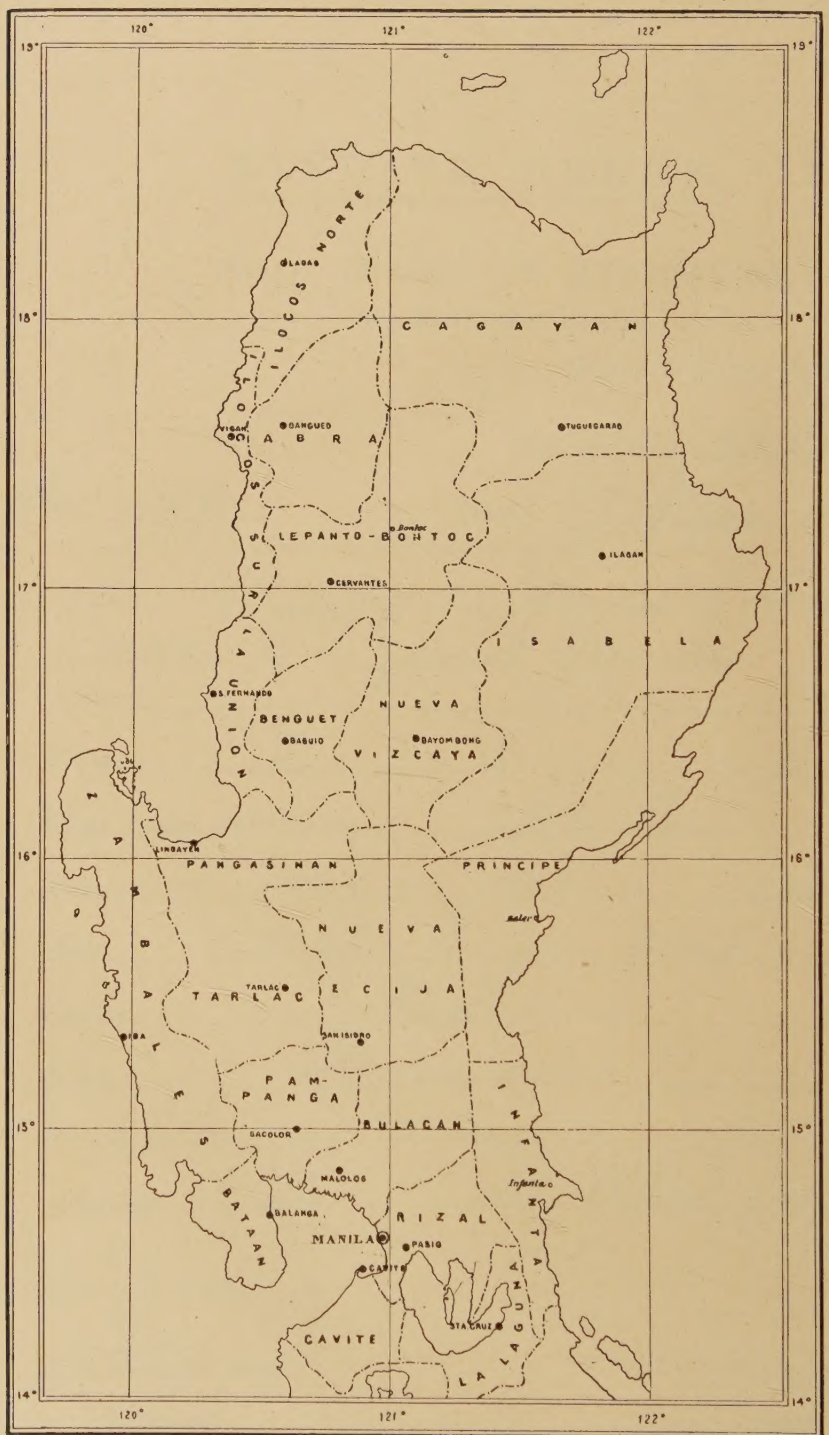
120°
121°
122°
19°
18°
17°
16°
15°
14°
ILOCOS NORTE
LAOAG
CAGAYAN
ABRA
BANGUED
TUGUEGARAO
LEPANTO-BONTOC
Bontoc
ILAGAN
CERVANTES
ISABELA
NUEVA VIZCAYA
BENGUET
BAGUIO
BAYOMBONG
LINGAYEN
PANGASINAN
PRINCIPE
NUEVA ECIJA
TARLAC
SAN ISIDRO
PAMPANGA
BULACAN
MALOLOS
RIZAL
MANILA
PASIG
CAVITE
STA. CRUZ
LAGUNA
Infanta

PLATE I.